CHEMICAL INDUSTRIES
A Series of Reference Books and Textbooks

Founding Editor

HEINZ HEINEMANN
Berkeley, California

Series Editor

JAMES G. SPEIGHT
CD & W, Inc.
Laramie, Wyoming

MOST RECENTLY PUBLISHED

Advances in Refining Catalysis, Deniz Uner
Handbook of Petroleum Refining, James G. Speight
Handbook of Refinery Desulfurization, Nour Shafik El-Gendy and James G. Speight
    Mohamed A. Aggour, and Mohamed A. Fahim
Refining Used Lubricating Oils, James Speight and Douglas I. Exall
The Chemistry and Technology of Petroleum, Fifth Edition, James G. Speight
Transport Phenomena Fundamentals, Third Edition, Joel Plawsky
Synthetics, Mineral Oils, and Bio-Based Lubricants: Chemistry and Technology,
Modeling of Processes and Reactors for Upgrading of Heavy Petroleum,
    Jorge Ancheyta
Fundamentals of Automatic Process Control, Uttam Ray Chaudhuri
    and Utpal Ray Chaudhuri
The Chemistry and Technology of Coal, Third Edition, James G. Speight
Practical Handbook on Biodiesel Production and Properties, Mushtaq Ahmad,
    Mir Ajab Khan, Muhammad Zafar, and Shazia Sultana
Introduction to Process Control, Second Edition, Jose A. Romagnoli
    and Ahmet Palazoglu
Fundamentals of Petroleum and Petrochemical Engineering, Uttam Ray Chaudhuri
Advances in Fluid Catalytic Cracking: Testing, Characterization, and
    Environmental Regulations, edited by Mario L. Occelli
Advances in Fischer-Tropsch Synthesis, Catalysts, and Catalysis,
    edited by Burtron H. Davis and Mario L. Occelli
Transport Phenomena Fundamentals, Second Edition, Joel Plawsky
Asphaltenes: Chemical Transformation during Hydroprocessing of Heavy Oils,
    Jorge Ancheyta, Fernando Trejo, and Mohan Singh Rana
Contents

Preface ................................................................................................................................................................................ix
Contributors ........................................................................................................................................................................... xi

SECTION I  Deposit Control Additives: Oxidation Inhibitors

Chapter 1  Antioxidants ......................................................................................................................................................... 3
   Robert G. Rowland, Jun Dong, and Cyril A. Migdal

Chapter 2  Zinc Dithiophosphates ...................................................................................................................................... 37
   Randolf A. McDonald

Chapter 3  Dispersants .......................................................................................................................................................... 45
   Syed Q.A. Rizvi

Chapter 4  Detergents ............................................................................................................................................................ 67
   Philip Ma

SECTION II  Film-Forming Additives

Chapter 5  Organic Friction Modifiers ............................................................................................................................... 87
   Dick Kenbeck and Thomas F. Bunemann

Chapter 6  Selection and Application of Solid Lubricants as Friction Modifiers ................................................................. 99
   Gino Mariani

SECTION III  Antiwear and Extreme Pressure (EP) Additives

Chapter 7  Ashless Antiwear and Antiscuffing (Extreme Pressure) Additives ................................................................. 117
   Liehpao Oscar Farng and Tze-Chi Jao

Chapter 8  Ashless Phosphorus–Containing Lubricating Oil Additives .............................................................................. 157
   W. David Phillips and Neal Milne

Chapter 9  Sulfur Carriers ...................................................................................................................................................... 197
   Thomas Rosserucker, Sandra Horstmann, and Achim Fessenbecker

Chapter 10 Chlorinated Paraffins ....................................................................................................................................... 219
   James MacNeil
SECTION IV  Viscosity Control Additives

Chapter 11  Olefin Copolymer Viscosity Modifiers ................................................................. 225  
  Michael J. Covitch

Chapter 12  Polymethacrylate Viscosity Modifiers and Pour Point Depressants  ................. 247  
  Boris M. Eisenberg, Alan Flamberg, and Bernard G. Kinker

Chapter 13  Hydrogenated Styrene–Diene Copolymer Viscosity Modifiers ................................ 263  
  Isabella Goldmints and Sonia Oberoi

Chapter 14  Pour Point Depressants .................................................................................... 277  
  Joan Souchik

SECTION V  Miscellaneous Additives

Chapter 15  Evaluating Tackiness of Polymer-Containing Lubricants by Open-Siphon Method: Experiments, Theory, and Observations ................................................................. 291  
  Brian M. Lipowski and Daniel M. Vargo

Chapter 16  Seal Swell Additives .......................................................................................... 303  
  Ronald E. Zielinski and Christa M.A. Chilson

Chapter 17  Antimicrobial Additives for Metalworking Lubricants ........................................ 309  
  Alan C. Eachus and William R. Schwingel

Chapter 18  Surfactants in Lubrication .................................................................................. 321  
  Girma Biresaw

Chapter 19  Foaming Chemistry and Physics ......................................................................... 337  
  Kalman Koczo, Mark D. Leatherman, Kevin Hughes, and Don Knobloch

Chapter 20  Antifoams for Nonaqueous Lubricants .............................................................. 385  
  Ernest C. Galgoci

Chapter 21  Corrosion Inhibitors and Rust Preventatives ....................................................... 393  
  Michael T. Costello

Chapter 22  Alkylated Naphthalenes .................................................................................... 409  
  Maureen E. Hunter

Chapter 23  Additives for Bioderived and Biodegradable Lubricants ...................................... 421  
  Mark Miller
SECTION VI  Applications

Chapter 24  Additives for Grease Applications................................................................. 431
            Robert Silverstein and Leslie R. Rudnick

Chapter 25  Additives for Crankcase Lubricant Applications ........................................ 447
            Ewa A. Bardasz and Gordon D. Lamb

Chapter 26  Additives for Industrial Lubricant Applications.......................................... 473
            Leslie R. Rudnick

Chapter 27  Lubricants and Fluids for the Food Industry ............................................. 485
            Saurabh Lawate

Chapter 28  Lubricants for the Disk Drive Industry ....................................................... 503
            Tom E. Karis

SECTION VII  Trends

Chapter 29  Impacts of the Globally Harmonized System on Lubricant Manufacturers........ 561
            Luc Séguin

Chapter 30  Long-Term Trends in Industrial Lubricant Additives..................................... 571
            Fay Linn Lee and John W. Harris

Chapter 31  Long-Term Additive Trends in Aerospace Applications............................. 589
            Carl E. Snyder, Jr., Lois J. Gschwender, and Shashi Kant Sharma

Chapter 32  Eco Requirements for Lubricant Additives and Base Stocks......................... 597
            Thomas Rühle and Matthias Fies

SECTION VIII  Methods and Resources

Chapter 33  Lubricant Industry–Related Terms and Acronyms......................................... 623
            Leslie R. Rudnick

Chapter 34  Testing Methods for Additive/Lubricant Performance................................ 635
            Leslie R. Rudnick

Chapter 35  Internet Resources for the Additive/Lubricant Industry............................. 647
            Leslie R. Rudnick

Appendix A: Grease Compatibility Chart ...................................................................... 677
Appendix B: Color Scale Comparison Chart .................................................................. 679
Appendix C: ISO Viscosity Ranges ............................................................................... 681
Index ......................................................................................................................... 683
Lubricant additives continue to be developed to improve the properties and performance of modern lubricants. The market for passenger car and heavy-duty motor oils, industrial oils, and metalworking fluids is growing rapidly, and this growth is expected to continue. Additional additive technology needs to be developed to meet performance requirements and the increased demand, especially in the Asia-Pacific region. China and India, for example, represent highly populated markets that are continuing to grow in infrastructure, leading to a growth in industrial equipment and number of vehicles. Many U.S. and EU companies continue to retain their presence in the Asia-Pacific region through either new manufacturing facilities or sales and distribution offices.

This edition includes new chapters on chlorohydrocarbons, foaming chemistry and physics, antifoams for nonaqueous lubricants, hydrogenated styrene–diene viscosity modifiers, alkylated aromatics, and the impact of REACh (Registration, Evaluation, Authorisation and Restriction of Chemicals) and GHS (Global Harmonized System) on the lubricant industry. In addition, many chapters from the previous edition have new coauthors and have been updated since then.

Environmental issues and applications that require lubricants to operate under severe conditions cause an increase in the use of synthetics. Owing to performance and maintenance reasons, many applications that have historically relied on petroleum-derived lubricants are shifting to synthetic lubricant–based products. Cost issues, on the contrary, tend to shift the market toward group II and III base oils where hydrocarbons can be used. A shift to renewable and biodegradable fluids is also necessary, and this will require a greater need for new effective additives to meet the challenges of formulating lubricants for various applications.

There are several indications that the lubricant additive industry will grow and change.

Legislation is driving changes to fuel composition and lubricant components, and, therefore, future lubricant developments will be constrained compared to what has been done in the past. REACh in the EU is placing constraints on the incentive to develop new molecules that will serve as additives. The cost of introduction of new proprietary materials will be the burden of the company that develops the new material. The costs in generating any needed data on the toxicology or biodegradability of the materials for many common additives that are produced by several manufacturers will be shared among them.

Continued progress toward new engine oil requirements will require oils to provide improved fuel economy and to have additive chemistry that does not degrade emission system components. This will require a new test to evaluate the volatility of phosphorus in engine oils and to improve oil properties in terms of protecting the engine. Future developments and requirements will undoubtedly require new, more severe testing protocols.

More advanced technologies will require the application of new types of lubricants, containing new additive chemistries required for the exploration of space and oceans. Since these remote locations and extreme environments require low maintenance, they will place new demands on lubricant properties and performance.

This book would not have developed the way it has without the invaluable help and encouragement of many of my colleagues. I thank all of the authors of the chapters contained herein for responding to the deadlines. There is always a balance between job responsibilities and publishing projects like this one. I truly appreciate all of their effort toward this new edition. It is your contributions that have created this resource for our industry.

I especially thank Barbara (Glunn) Knott at Taylor & Francis Group, with whom I have worked earlier on Synthetics, Mineral Oils, and Bio-Based Lubricants, for her support to this project from its early stages through its completion. I also thank Cheryl Wolf, Editorial Assistant, Joette Lynch, Project Editor, and Vinithan Sethumadhavan, Account Manager at SPI, who have been invaluable in every way in the progress of this project and have been a tremendous asset to me as an editor and helpful to the many contributors of this book.

I also thank my wife, Paula, and our children, Eric and Rachel, for all their support during this project.

Dr. Leslie R. Rudnick
Designed Materials LLC, Scottsdale, Arizona
Contributors

Ewa A. Bardasz
ZUAL Associates in Lubrication, LLC
Mentor, Ohio

Girma Biresaw
Cereal Products and Food Science Research Unit
NCAUR-MWA-ARS-USDA
Peoria, Illinois

Thomas F. Bunemann
Uniqema
Gouda, the Netherlands

Christa M.A. Chilson
PolyMod® Technologies, Inc.
Fort Wayne, Indiana

Michael T. Costello
BASF Corporation
Tarrytown, New York

Michael J. Covitch
The Lubrizol Corporation
Wickliffe, Ohio

Jun Dong
Chemtura Corporation
Middlebury, Connecticut

Alan C. Eachus
Independent Consultant
Villa Park, Illinois

Boris M. Eisenberg
Evonik Oil Additives
Darmstadt, Germany

Liehpaо Oscar Farng
ExxonMobil Research and Engineering Company
Paulsboro, New Jersey

Achim Fessenbecker
Rhein Chemie Rheinau GmbH
Mannheim, Germany

Matthias Fies
BASF SE
Ludwigshafen, Germany

Alan Flamberg
Evonik Oil Additives USA, Inc.
Horsham, Pennsylvania

Ernest C. Galgoci
Münzing North America, LP
Bloomfield, New Jersey

Isabella Goldmints
Infineum USA L.P.
Linden, New Jersey

Lois J. Gschwender
University of Dayton Research Institute
Nonstructural Materials Division
Dayton, Ohio

John W. Harris (deceased)
Shell Global Solutions
Houston, Texas

Sandra Horstmann
Lanxess Deutschland GmbH
Cologne, Germany

Kevin Hughes
The Lubrizol Corporation
Wickliffe, Ohio

Maureen E. Hunter
King Industries, Inc.
Norwalk, Connecticut

Tze-Chi Jao
Afton Chemical Corporation
Richmond, Virginia

Tom E. Karis
Independent Consultant
Aromas, California

Dick Kenbeck
Uniqema
Gouda, the Netherlands

Bernard G. Kinker
Independent Consultant
Kintnersville, Pennsylvania

Don Knobloch
The Lubrizol Corporation
Wickliffe, Ohio

Kalman Koczo
Momentive Performance Materials
Tarrytown, New York
Contributors

Gordon D. Lamb
Lubrizol Limited
Hazelwood, United Kingdom

Saurabh Lawate
The Lubrizol Corporation
Wickliffe, Ohio

and
CPI Fluid Engineering
Division of the Lubrizol Corporation
Berkshire Hathaway Company
Midland, Michigan

Mark D. Leatherman
Momentive Performance Materials
Tarrytown, New York

Fay Linn Lee
Shell Lubricants
Houston, Texas

Brian M. Lipowski
Avery Dennison Performance Tapes
Painesville, Ohio

Philip Ma
BASF Corporation
Tarrytown, New York

James MacNeil
Qualice LLC
Hamlet, North Carolina

Gino Mariani
National Starch and Chemical Company
Port Huron, Michigan

Randolf A. McDonald
Functional Products, Inc.
Cleveland, Ohio

Cyril A. Migdal
LanXess Solutions US, Inc.
Naugatuck, Connecticut

Mark Miller
RSC Bio Solutions
Indian Trail, North Carolina

Neal Milne
Chemtura Petroleum Additives
Manchester, United Kingdom

Sonia Oberoi
Infineum USA L.P.
Linden, New Jersey

W. David Phillips
Independent Consultant
Poynton
Cheshire, United Kingdom

Syed Q.A. Rizvi
Research and Development
Elevance Renewable Sciences, Inc.
Woodridge, Illinois

Thomas Rossrucker
Lanxess Deutschland GmbH
Cologne, Germany

Robert G. Rowland
LanXess Solutions US, Inc.
Naugatuck, Connecticut

Leslie R. Rudnick
Designed Materials LLC
Scottsdale, Arizona

Thomas Rühle
BASF SE
Ludwigshafen, Germany

William R. Schwingel
Masco Corporation
Taylor, Michigan

Luc Séguin
KMK Regulatory Services, Inc.
Quebec, Canada

Shashi Kant Sharma (Retired)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base Ohio
Ohio

Robert Silverstein
The Orelube Corporation
Bellport, New York
Contributors

Carl E. Snyder, Jr.
University of Dayton Research Institute
Nonstructural Materials Division
Dayton, Ohio

Joan Souchik
Evonik Oil Additives USA, Inc.
Horsham, Pennsylvania

Daniel M. Vargo
Functional Products Inc.
Macedonia, Ohio

Ronald E. Zielinski
PolyMod® Technologies, Inc.
Fort Wayne, Indiana
Section I

Deposit Control Additives
Oxidation Inhibitors
1 Antioxidants

Robert G. Rowland, Jun Dong, and Cyril A. Migdal

CONTENTS

1.1 Introduction ................................................................. 4
1.2 Sulfur Compounds ......................................................... 4
1.3 Sulfur–Nitrogen Compounds ......................................... 5
1.4 Phosphorus Compounds ............................................... 6
1.5 Sulfur–Phosphorus Compounds .................................. 7
1.6 Amine and Phenol Derivatives ..................................... 7
   1.6.1 Aromatic Amine Compounds .................................. 8
   1.6.2 Hindered Phenolic Compounds ............................... 10
   1.6.3 Multifunctional Amine and Phenol Derivatives .......... 13
1.7 Organocopper Antioxidants .......................................... 13
1.8 Boron Antioxidants ...................................................... 13
1.9 Miscellaneous Organometallic Compounds ..................... 14
1.10 Controlled Release Antioxidants .................................. 15
1.11 Mechanisms of Hydrocarbon Oxidation and Antioxidant Action .................................................. 15
   1.11.1 Autoxidation of Lubricating Oil .............................. 15
       1.11.1.1 Initiation ...................................................... 15
       1.11.1.2 Chain Propagation ..................................... 15
       1.11.1.3 Chain Branching ....................................... 15
       1.11.1.4 Chain Termination ..................................... 16
   1.11.2 Metal-Catalyzed Lubricant Degradation ................ 16
       1.11.2.1 Metal Catalysis ......................................... 16
   1.11.3 High-Temperature Lubricant Degradation ............... 16
   1.11.4 Effect of Base Oil Composition on Oxidative Stability ................................................................. 16
   1.11.5 Oxidation Inhibition ............................................ 17
   1.11.6 Mechanisms of Primary Antioxidants ..................... 17
       1.11.6.1 Hindered Phenolics .................................... 17
       1.11.6.2 Aromatic Amines ....................................... 18
   1.11.7 Mechanisms of Secondary Antioxidants ................ 20
       1.11.7.1 Organosulfur Compounds .............................. 20
       1.11.7.2 Organophosphorus Compounds ..................... 20
   1.11.8 Antioxidant Synergy ............................................ 21
1.12 Oxidation Bench Tests .............................................. 21
   1.12.1 Thin-Film Oxidation Tests .................................... 23
       1.12.1.1 Pressurized Differential Scanning Calorimetry (PDSC) ...................................................... 23
       1.12.1.2 Thermo-Oxidation Engine Oil Simulation Test (TEOST, ASTM D6335; D7097) .................. 23
       1.12.1.3 Thin-Film Oxygen Uptake Test (TFOUT, ASTM D4742) .................................................... 23
   1.12.2 Bulk Oil Oxidation Tests ..................................... 23
       1.12.2.1 Turbine Oil Stability Test (TOST, ASTM D943, D4310, Dry TOST D7873) ......................... 23
       1.12.2.2 IP 48 Method ............................................. 24
       1.12.2.3 IP 280/CIGRE ........................................... 24
   1.12.3 Oxygen Uptake Test .......................................... 24
       1.12.3.1 Rotating Pressure Vessel Oxidation Test (RPVOT, ASTM D2272) .................................. 24
   1.12.4 Experimental Observations .................................. 24
1.13 Antioxidant Performance with Base Oil Selection ........... 26
1.14 Future Requirements .................................................. 27
1.15 Some Commercial Antioxidants .................................. 28
1.16 Some Commercial Metal Deactivators ........................... 28
References ........................................................................ 29
1.1 INTRODUCTION

Well before the mechanism of hydrocarbon oxidation was thoroughly investigated, researchers had come to understand that some oils provided greater resistance to oxidation than others. The difference was eventually identified as being due to naturally occurring antioxidants, which varied depending upon the nature of the crude oil, and refining techniques. Some of these natural antioxidants were found to contain sulfur- or nitrogen-bearing functional groups. Therefore, it is not surprising that certain additives that are used to impart special properties to the oil, such as sulfur-bearing chemicals, were found to provide additional antioxidant stability. The discovery of sulfurized additives providing oxidation stability was followed by the identification of similar properties with phenols, which led to the development of sulfurized phenols. Next, certain amines and metal salts of phosphorus-or sulfur-containing acids were identified as imparting oxidation stability. Numerous antioxidants for lubricating oils have been patented and described in the literature. Today, nearly all lubricants contain at least one antioxidant. Since oxidation is the primary cause of oil degradation, improving oxidative stability is critical to achieving extended drain intervals.

Lubricant oxidation is initiated by the exposure of hydrocarbons to oxygen and heat. Oxidation can be greatly accelerated by the presence of transition metals such as copper, iron, and nickel. The internal combustion engine is an excellent chemical reactor for catalyzing the process of oxidation with heat and engine metal parts acting as effective oxidation catalysts. Thus, in-service engine oils are probably exposed to more oxidative stress than are encountered in most other lubricant applications. Antioxidant additives protect the lubricant from oxidative degradation, allowing the fluid to meet the demanding requirements for use in engines and industrial applications.

Numerous effective antioxidant classes have been developed over the years and have seen use in engine oils, automatic transmission fluids, gear oils, turbine oils, compressor oils, greases, hydraulic fluids, and metal working fluids. The main classes include oil-soluble organic and organometallic antioxidants of the following types:

- Sulfur compounds
- Sulfur–nitrrogen compounds
- Phosphorus compounds
- Sulfur–phosphorus compounds
- Aromatic amine compounds
- Hindered phenolic compounds
- Multifunctional amine and phenol derivatives
- Organocopper compounds
- Boron compounds
- Other organometallic compounds
- Controlled release antioxidants

These additive types will be discussed in the following. However, it is important to remember that while sulfur, phosphorus, and various metal-containing additives can impart antioxidant and antiwear benefits to engine oils, they are often at odds with recent environmental regulations requiring reduction in SO2, NOx, and soot emissions. Following the drastic regulatory reductions in the allowable sulfur content of fuels, limits are also set on the amounts of sulfated ash, phosphorus, and sulfur (SAPS) that can be present in an oil. This is done to protect emissions after-treatment devices such as catalytic converters and diesel particulate filters that can be damaged by SAPS [1]. Hence, the trend is toward employing ashless antioxidants, which do not contain sulfur or phosphorus. Various formulations have been proposed to address this problem [2–5].

1.2 SULFUR COMPOUNDS

The initial concepts of using antioxidants to inhibit oil oxidation date back to the 1800s. One of the earliest lubricant inventions described in the literature [6] is the heating of a mineral oil with elemental sulfur to produce a nonoxidizing oil. However, the major drawback to this approach is the high corrosivity of the sulfurized oil toward copper. An engine lubricant with antioxidant and corrosion inhibition characteristics was obtained from sulfurizing terpenes [7]. Paraffin wax has also been employed to prepare sulfur compounds [8–11].

Aromatic sulfides represent another class of sulfur additive used as oxidation and corrosion inhibitors. Examples of simple sulfides are dibenzyl sulfide and dixylyl disulfide. Mono- and dialkyl diphenyl sulfides obtained by reacting diphenyl sulfide with C10–C18 α-olefins in the presence of aluminum chloride have been demonstrated to be powerful antioxidants for high-temperature lubricants, especially those utilizing synthetic base oils such as hydrogenated poly-α-olefins (PAOs), diesters, and polyol esters [12]. The hydroxyl groups of the alkyl phenol sulfides may also be treated with metals to form oil-soluble metal phenates. These metal phenates function as both detergents and antioxidants.

Representative structures of several sulfur compounds are illustrated in Figure 1.1. The actual additives can be chemically complex mixtures. Hindered phenols that contain sulfur will be discussed further in Section 1.6.2.

Multifunctional antioxidant and extreme pressure additives with heterocyclic structures were prepared by sulfurizing norbornene, 5-vinylnorbornene dicyclopentadiene, or methyl cyclopentadiene dimer [13]. Heterocyclic compounds such as n-alkyl 2-thiazoline disulfide in combination with ZDDP exhibited excellent antioxidant performance in laboratory engine tests [14]. Heterocyclic sulfur- and oxygen-containing compositions derived from mercaptopentothiazole and β-thiodialkanol have been found to be excellent antioxidants in automatic transmission fluids [15]. Novel antioxidant and antiwear additives based on dihydrobenzothiophenes have been prepared via condensation of low-cost aryl thiols and carbonyl compounds in a high-yield one-step process [16].
Antioxidants

1.3 SULFUR–NITROGEN COMPOUNDS

Dithiocarbamates were first introduced in the early 1940s as fungicides and pesticides [17]. Their potential use as antioxidants for lubricants was not realized until the mid-1960s [18], and since then, there has been continuous interest in this type of chemistry for lubricant applications [19]. Today, dithiocarbamates represent a main class of sulfur–nitrogen-bearing compounds being used as antioxidant, antiwear, and anticorrosion additives for lubricants.

Depending upon the type of adduct to the dithiocarbamate core, ashless and metal-containing dithiocarbamate derivatives can be formed. Typical examples of ashless materials are methylene bis(dialkyldithiocarbamate) and dithiocarbamate esters with general structures being illustrated in Figure 1.2. Both are synergistic with alkylated diphenylamine and organo-molybdenum compounds in high-temperature deposit control [20]. In particular, methylene bis(dialkyldithiocarbamate) in combination with primary antioxidants such as arylamines or hindered phenolics and triazole derivatives is known to provide synergistic action in stabilizing mineral oils and synthetic lubricating oils [21–23]. This material has been used to improve antioxidation characteristics of internal combustion engine oils containing low levels (less than 0.1 wt%) of phosphorus [2].

It has been known that metal dithiocarbamates such as zinc, copper, lead, antimony, bismuth, and molybdenum dithiocarbamates possess desirable lubricating characteristics including antiwear and antioxidant properties. The associated metal ions affect the antioxidancy of the additives. Molybdenum dithiocarbamates are the most commercially important of the group and are widely used in engine crankcase lubricants. Certain molybdenum additives, which impart good oxidation resistance and have acceptable corrosion characteristics, are prepared by reacting water, an acidic molybdenum compound, a basic nitrogen complex, and a sulfur source [24,25]. Oil-soluble trinuclear molybdenum dithiocarbamates prepared by reacting ammonium polythiomolybdate with appropriate tetraalkylthiuram disulfides were found to be superior to dinuclear molybdenum compounds in terms of providing lubricant antioxidant, antiwear, and friction-reducing properties [26].

When combined with an appropriate aromatic amine, molybdenum dithiocarbamates can exhibit synergistic antioxidant effects in oxidation tests [27]. As a result, molybdenum dialkyldithiocarbamates (C$_7$–C$_{24}$) and alkylated diphenylamines are claimed broadly for lubricating oils [28]. More restrictive are claims for molybdenum dialkyldithiocarbamates (C$_8$–C$_{23}$ and/or C$_{17}$–C$_{38}$) and alkylated diphenylamines in lubricating oils that contain less than 3 wt% of aromatic content and less than 50 ppm of sulfur and nitrogen [29]. Molybdenum dithiocarbamate was used to top treat engine oils formulated with Group I base oils (>300 ppm S) and an additive package designed for Group II base oils. The oils passed the Sequence IIIF oxidation test, in which the oils would otherwise fail without the molybdenum top treatment [30]. Further demonstrated is a combination of alkylated diphenylamines, sulfurized olefin or hindered phenolic, and oil-soluble molybdenum compounds including molybdenum dithiocarbamate. The mixture is highly effective in stabilizing lubricants, especially those formulated with highly saturated, low-sulfur base oils [31].

FIGURE 1.1 Examples of antioxidants containing sulfur.

FIGURE 1.2 Ashless dithiocarbamates for lubricants.
Thiadiazole derivatives, particularly the monomers and dimers, represent another class of sulfur- and nitrogen-bearing multifunctional additives with antioxidant activity. For example, a monomeric 2-alkylesterthio-5-mercaptop-1,3,4-thiadiazole has been reported to increase the oxidative stability of engine oils under thin-film oxidation conditions as measured by the Thin-Film Oxygen Uptake Test (TFOUT, ASTM D7098) [32]. Lithium 12-hydroxystearate grease containing the dimer 2,5-dithiobis(1,3,4-thiadiazole-2-thiol) exhibited superior oxidative stability in the ASTM D942 pressure vessel oxidation method [33]. When used in conjunction with alkylated diphenylamine and organomolybdenum compound, the thiadiazole derivative improved the Thermo-Oxidation Engine Oil Simulation Test (TEOST®, ASTM D7097) deposits relative to a control engine oil [34]. In addition to providing antioxidant benefit, the thiadiazole derivatives have been widely used as ashless antiwear and extreme pressure additives. Some of them can also provide corrosion inhibition and metal deactivation properties to nonferrous metals such as copper.

Alkylated phenothiazines are also well-known antioxidants containing sulfur and nitrogen, which have been used to stabilize ester-based aviation fluids [35] and engine oils [36]. They are usually prepared by sulfurization of alkylated diphenylamines [37] and are frequently used in combination with the parent alkylated diphenylamines [38]. A recent study found that in PAO, dioctylphenothiazine gave better control of total acid number and viscosity than dioctyldiphenylamine, but significantly worse deposits. A synergistic 1:1 mixture of the two components gave satisfactory results in all three tests [39]. N-substituted phenothiazines (especially N-alkylthioethyl) have been claimed as having improved antioxidant activities [40]. Functionalized phenothiazines together with aromatic amines can be attached to olefin copolymers resulting in a multifunctional antioxidant, antiwear agent, and viscosity index improver for lubricants [41].

Diamine sulfides, including diamine polysulfides, can also provide effective oxidation control when used in conjunction with oil-soluble copper. In demonstration, dimorpholine disulphide and (dimethyl morpholine) disulphide were compared to primary alkyl ZDDP and found to be superior in controlling oil viscosity increase of engine crankcase lubricants at elevated temperatures [42].

### 1.4 PHOSPHORUS COMPOUNDS

The good performance of phosphorus as an oxidation inhibitor in oils was one of the earliest improvements in the development of additive formulated lubricants. The use of elemental phosphorus to reduce sludge formation in oils was described in 1917 [43]. However, elemental phosphorus, like elemental sulfur, has poor solubility in oil and may have corrosive side effects to many nonferrous metals and alloys, so it is rarely incorporated in oils in this form. Oil-soluble organic compounds of phosphorus are preferred instead. Naturally occurring phosphorus compounds such as lecithin have been utilized as antioxidants, and many patents have been issued on these materials for use alone or in combination with other additives [42–47]. Lecithin is a phosphatide that has been produced commercially as a by-product from the processing of crude soybean oil.

The antioxidant properties of synthetic neutral and acid phosphate esters have been known for some time. Alkyl and aryl phosphites, such as tributyl phosphate and triphenyl phosphate, are efficient antioxidants in some petroleum base oils, and many patents have been issued on such compositions [48,49]. Table 1.1 summarizes the patenting activities of the last 45 years on the stabilization of various lubricants with organophosphites.

<table>
<thead>
<tr>
<th>Applications</th>
<th>Phosphites</th>
<th>Supplementary Antioxidants</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressor oils</td>
<td>Trinyonylphenyl phosphate; tributyl phosphate; tridecylphosphate; triphenyl phosphate; trioctylphosphate; dilaurylphosphate</td>
<td>Secondary aminic and hindered phenolic</td>
<td>[53]</td>
</tr>
<tr>
<td>Automotive and industrial lubricants</td>
<td>Triarylphtohosphate; trialkylphosphates; alkyl aryl phosphates; acid dialky phosphites</td>
<td>Secondary aminic and hindered phenolic</td>
<td>[54]</td>
</tr>
<tr>
<td>Automotive and industrial lubricants</td>
<td>Triphenyl phosphate; diisodecyl pentaerythritol diphosphate; tri-isodecyl pentaaryl phosphate; dilauryl phosphate</td>
<td>Secondary aminic and hindered phenolic</td>
<td>[55]</td>
</tr>
<tr>
<td>Hydraulic fluids, steam turbine oils, compressor oils, and heat transfer oil</td>
<td>Steric hindered tributyl phosphate; bis(butylphenyl pentaerythritol) diphosphate</td>
<td>(3,5-Di-tet-butyl)4-hydroxybenzyl isocyanurate</td>
<td>[50]</td>
</tr>
<tr>
<td>Steam turbine oils, gas turbine oils</td>
<td>Triphenyl phosphate; trialkyl-substituted phenyl phosphate</td>
<td>Alkylated diphenylamine; phenyl-naphthylamine</td>
<td>[56]</td>
</tr>
<tr>
<td>Hydraulic fluids, automatic transmission fluids</td>
<td>Trialkyl phosphites</td>
<td>Secondary aminic and hindered phenolic including bis-phenol</td>
<td>[57]</td>
</tr>
<tr>
<td>Lubricant base oils, polymers</td>
<td>4-Oxo-1,3-dioxo-2-phosphanaphthalenes</td>
<td>Alkylated diphenylamines and hindered phenolics</td>
<td>[58]</td>
</tr>
<tr>
<td>Internal combustion engines, steam and gas turbines</td>
<td>Diisodecyl pentaerythritol diphosphate</td>
<td>Alkylated diphenylamines and/or hindered phenolics</td>
<td>[59]</td>
</tr>
</tbody>
</table>
Antioxidants

For optimum antioxidant performance, phosphites are customarily blended with aminic or hindered phenolic antioxidants that can lead to synergistic effect. For better hydrolytic stability, trisubstituted phosphites with sterically hindered structures such as tris(2,4-di-tert-butylphenyl) phosphate and those based on pentaerythritol, as described in the U.S. Patent 5,124,057 [50], are preferred. The aluminum, calcium, or barium salts of alkyl phosphoric acids are another type of phosphorus compound that displays antioxidant properties [51,52].

1.5 SULFUR-PHOSPHORUS COMPOUNDS

The most widely used class of sulfur–phosphorus additives is the metal dialkyldithiophosphates. Metal dithiophosphates are typically prepared by the reaction of phosphorus pentasulfide with alcohols to form dithiophosphoric acids, followed by neutralization of the acids with an appropriate metal oxide compound. Most readily available simple C_{2}–C_{18} alcohols, such as 1-hexanol, 2-ethylhexanol, 2-octanol, 2-butanol, cyclohexanol, phenol, and 4-nonylphenol, have been used in these reactions [60,61]. For the second reaction step, zinc, molybdenum, or barium oxides are usually chosen.

Providing both antioxidant and antwear/Extreme Pressure activity, the zinc diorganodithiophosphates [62] (ZDDPs) have collectively been the most important multifunctional lubricant additive since the 1940s. (In historical usage, ZDDP is a broad term that is generally understood to include zinc dialkyldithiophosphates, zinc dialkyldithiophosphates, and any alkyl permutations thereof.) Functioning as peroxide decomposers [1], ZDDPs have been some of the most cost-effective antioxidants and therefore since their discovery have been included as a key component in many oxidation inhibitor packages for engine oils and transmission fluids. While zinc diorganodithiophosphates provide a valuable antioxidant credit, they are far more important to lubricant formulators for the very cost-effective antwear protection that they offer.

Unfortunately, zinc diorganodithiophosphates can decompose to form volatile phosphorus species, which over time can coat and clog the supporting media in catalytic converters. When phosphorus was first implicated as causing this problem, a great deal of effort was expended toward the goal of entirely removing zinc diorganodithiophosphates from engine oils [1]. Because of concerns about retaining critical antwear protection, most engine manufacturers have preferred to compromise by using oils with reduced phosphorus levels while designing zinc diorganodithiophosphates that form lesser amounts of volatile phosphorus upon decomposition [60,62,63]. The zinc diorganodithiophosphates prepared from 4-methyl-2-pentanol or 2-ethylhexanol have been identified as being particularly nonvolatile [60].

Many descriptions have recently appeared of organomolybdenum phosphorodithioate complexes that impart excellent oxidation stability to lubricants. In certain circumstances, oil-soluble molybdenum compounds are preferred additives owing to their multifunctional characteristics such as antwear, extreme pressure, antioxidant, antipitting, and antifriction properties. For instance, several molybdenum dialkylphosphorodithioate complexes with varying alkyl chains (e.g., pentyl, octyl, 2-ethylhexyl, and isodecyl) were reported to exhibit appreciable antioxidation, antwear, and antifriction properties [64]. Novel trinuclear molybdenum dialkyldithiophosphates prepared by reacting an ammonium polythiomolybdate and an appropriate bisalkyldithiophosphoric acid possess excellent antioxidant as well as antwear and friction-reducing properties [26]. Some molybdenum compounds have been used commercially in engine oils and metal working fluids as well as in a variety of industrial and automotive lubricating oils, greases, and specialties [65]. The combination of ZDDP with a molybdenum-containing adduct, prepared by reacting a phosphosulfurized polyisooalkylene or α-olefin with a molybdenum salt, has been described [66]. In this case, the molybdenum adduct alone gave poor performance in oxidation tests, but the mixture with ZDDP provided good oxidation stability. Novel organomolybdenum complexes prepared with vegetable oil have been identified as being synergistic with alkylated diphenylamines and ZDDPs in lubricating oils [67].

Due to increasing concerns about the use of metal dithiophosphates that are related to toxicity, waste disposal, filter clogging, and pollution, etc., there have been extensive research activities on the use of ashless technologies for both industrial and automotive applications. A number of ashless compounds based on derivatives of dialkylyphosphorodithioic acids had been reported as multifunctional additives. Upon reacting diisooamylphosphorodithioic acid with various primary and secondary amines, eight alkylamino phosphorodithioates with varying chain length from C_{8} to C_{18} were obtained and found to possess excellent antwear and antioxidant properties as compared to ZDDP [68]. Alkylamino phosphorodithioates obtained from reacting heptylated, octylated, or nonylated phosphorodithioic acids with ethylene diamine, morpholine, or tert-alkyl (C_{12}–C_{14}) amines have been demonstrated to impart similar antioxidant and antwear efficacy and superior hydrolytic stability over ZDDP [69]. Phosphorodithioate ester derivatives containing a hindered phenol moiety are also known to have antioxidant potency. This type of chemistry can be obtained by reacting metal salts of phosphorodithioic acids with hindered phenol halides [70] or with hindered phenol aldehydes [71]. Substituting the phenol aldehydes with hindered cyclic aldehydes, in which the carbon atom attached to the carbonyl carbon contains no hydrogen atoms, may also result in products having excellent antioxidant and thermal stability characteristics [72].

1.6 AMINE AND PHENOL DERIVATIVES

Alkylated aromatic amines and hindered phenols are the most important single-purpose, ashless antioxidants in many lubricant applications today. It is highly unlikely that there is any engine oil, industrial turbine oil, or transmission fluid in use today that meets current industry specifications (SAE, ACEA, JASO, etc.) without containing one or more of these additives.

The introduction of aminic and phenolic antioxidants for engine oils began in the 1930s. In 1932, Standard Oil
applied for a patent that claims the use of alkylated phenolics as stabilizers for highly refined and hence readily oxidizable kerosene, mineral, and vegetable oils and fats [73]. In 1938, Gulf claimed dialkyl-cyclohexyl-phenols as stabilizers for hydrocarbon products, including gasoline, lubricating oils, and turbine oils [74]. Around the same time, alkylated aromatic amines were being developed as antioxidants for rubber [75]; and by the end of the decade, the utility of alkylated diphenylamines and phenyl-naphthylamines as stabilizers in rubber, gasoline, and oils was disclosed [76]. Aromatic amines and phenols were reacted together to form stabilizers for “gasoline inhibitors, high pressure lubricants, rubber antioxidants, etc.” [77].

With the intervention of World War II, many subsequent early advancements in lubricant antioxidant technology were undoubtedly made under the cloak of military secrecy. B.F. Goodrich received U.S. Patent 2,530,769 in 1950 for a liquid alkylated diphenylamine antioxidant for rubber, fatty oils, and petroleum oils [78]. While utility was only demonstrated for rubber in this patent, after 65 years this type of octylated, styrenated diphenylamine is still used as a lubricant antioxidant in certain markets.

1.6.1 **AROMATIC AMINE COMPOUNDS**

Alkylated diphenylamines are one of the most important classes of amine antioxidants being used today. While diphenylamine is an effective antioxidant by itself, only alkylated forms are suitable for use in lubricants. Alkylation improves the oil solubility of the fresh antioxidant and highly polar, oxidized products that are produced as the antioxidant is consumed. Increasing molecular weight reduces additive volatility, which is critical for retention of the antioxidant in the oil. Compared to diphenylamine, alkylated diphenylamines have markedly improved toxicological and environmental profiles.

Figure 1.3 illustrates a commercial route to the preparation of diphenylamine and the typical synthetic routes to some commonly used alkylated diphenylamines. The diphenylamine synthesis reactions start with benzene, which is first converted to nitrobenzene [79], followed by a high-temperature reduction to aniline [80]. Under very high-temperature (400°C–500°C) and high-pressure (50–150 psi) conditions, aniline can undergo a catalytic vapor-phase conversion to form diphenylamine [81].

To make alkylated diphenylamines, diphenylamine is reacted with an appropriate alkylating agent in the presence of an acidic catalyst. The alkylating agent is usually an olefin but can also be an alcohol, alkyl halide, or aliphatic carbonyl compound. From an economic viewpoint, the olefins are generally preferred. The most commonly used olefins are isobutylene (C4), diisobutylene (C8), propylene trimer (“nonenes,” C9), and propylene tetramer (C12).

Depending on the acidic catalyst, olefin, stoichiometry, and other reaction conditions, such as time and temperature, the degree of alkylation may progress from monodi- to trialkylation, and even some trialkylation may occur. Since the alkyl groups dilute the amount of functional diphenylamine that is present in the additive, overalkylation is to be avoided.

A number of commercial diphenylamine antioxidants have been prepared using diisobutylene as the alkylating olefin. Within a certain mole ratio range, diphenylamine can

![Figure 1.3](image_url) **FIGURE 1.3** Synthesis of diphenylamine and some alkylated diphenylamine antioxidants.
be reacted with diisobutylene at a temperature of 160°C or higher to facilitate chain scission of diisobutylene [82]. In the presence of an acid clay catalyst, the resulting product has less than 25% of 4,4′-diodicyldiphenylamine, which yields a liquid at room temperatures. In another process that involves two-step reactions [83], a light-colored liquid product is obtained by first reacting diphenylamine with diisobutylene, followed by reaction with a second more reactive olefin, for example, styrene, α-methylstyrene, or isobutylene. Specific mole ratios, reaction temperatures, and reaction durations are critical to obtain the desired alkylated diphenylamines [84]. U.S. Patent 6,355,839 [85] discloses a one-step process using highly reactive polysobutylene oligomers having an average molecular weight of about 160–280 Da and at least 25% of 2-methylvinylidenone isomers as the alkylating agents to make alkylated diphenylamines and other types of alkylated diarylamine. The resulting products are liquid at ambient temperatures.

Diphenylamine has been alkylated with PAOs of 120–600 Da. These PAOs are a by-product recovered from commercial PAO lubricant manufacture [86].

It was found that monosubstituted diphenylamines more readily oligomerize under a variety of conditions to produce higher-molecular-weight linear oligomers. Oligomers with 2–10 degrees of polymerization are desirable antioxidants especially for high-temperature applications. Disubstituted and polysubstituted diphenylamines, on the other hand, are more restricted from forming oligomers higher than dimers. Oligomeric versions of monosubstituted diphenylamine prepared from reacting diphenylamine with C₄–C₁₆ olefins have been described for use in ester lubricants [87]. The products are claimed to be more effective than simple diphenylamines for extremely high-temperature applications.

Substituted benzylamines or substituted 1-amino-1,2,3,4-tetrahydronaphthalene is particularly useful for synthetic lubricants such as PAOs or polyol esters. Oils bearing these additives demonstrate very low metal corrosion, low viscosity increase, and low sludge buildup [88]. Closely related mixed isomers of di(1,2,3,4-tetrahydro-naphthyl)amines are effective antioxidants for engine oils in the TEOST MHT™ (ASTM D7097) and for turbine oils in the Rotating Pressure Vessel Oxidation Test (RPVOT, ASTM D2272) [89].

A group of acridines, where one of the aromatic rings bears a fused ring substituent, have been claimed as antioxidants for lubricating oils [90]. Another group of novel substituted diphenylamines, where each phenyl ring bears a fused ring substituent, and the nitrogen is substituted with an allyl, benzyl, or methallyl group, have also been claimed as lubricant antioxidants [91]. Further improved antioxidant performance has been claimed when these compounds are used in combination with benzenamines such as dialkyl anilines or antranilic acid esters [92].

Alkylated phenyl-naphthylamines are another very important group of aminic antioxidants. While both the α- and β-isomers are effective antioxidants, only the phenyl-α-naphthylamine (PANA) derivatives are in use today, as the intermediate β-naphthylamine is a known carcinogen. Alkylated PANAs are significantly more expensive than alkylated diphenylamines. Therefore, PANAs are used primarily in particularly demanding high-temperature applications such as aviation lubricants [93,94].

Homo-oligomers of alkylated (C₄–C₉) diphenylamines, styrenated diphenylamines, or cross-oligomers of the alkylated diphenylamines with substituted PANA are claimed to possess superior antioxidant efficacy in synthetic ester lubricants for high-temperature applications [95]. Complex substituted PANA reaction products have been claimed to offer superior lubricant antioxidant performance over various closely related commercial alkylated diphenylamines and PANAs. The claimed products include materials prepared by using mixtures of propylene trimer with either α-methylstyrene or styrene to alkylate PANA, or a mixture of PANA and DPA [96].

A product made by reacting a polyalkylbenzaldehyde or anhydride first with an aromatic secondary amine and then with an alkanol amine was found to provide appreciable antioxidant, dispersancy, and anticorrosion effects to engine oils as tested in a Caterpillar engine test [97]. A more recent U.S. Patent [98] discloses materials made from the reaction of alkyl or alkenyl succinic acid derivative with a diamino-naphthyl compound for use as antioxidant, antitrust, and soot dispersing agents for lubricating oils. U.S. Patent 5,075,383 [99] describes novel antioxidant–dispersant additives obtained by reacting amino-aromatic polyamine compound, including aromatic secondary amines, with ethylene-propylene copolymer grafted with maleic anhydride. Engine oils containing the additives displayed improved performance characteristics in laboratory oxidation and sludge dispersancy tests as well as in the Sequence VE engine test.

Cross-products and co-oligomers of N-alkylated p-phenylenediamines with N-phenyl-α-naphthylamine have been claimed as antioxidants for liquid hydrocarbons and polyol esters [100]. Oligomeric products derived from thermal and chemical condensation of alkylated diphenylamine and alkylated PANA in the presence of aldehyde can provide high-performance and nonsludging attributes, as evident in the RPVOT, and in the ASTM D4310 sludging tendency test designed for turbine oils [101]. An antioxidant for ester-based chain lubricants has been claimed for oligomers of alkylated diphenylamines, alkylated PANAs, and their cross-products. The preferred aromatic amines are di-α-alkyl-diphenylamine and 4-α-alkyl-phenyl-α-naphthylamine [102]. The oligomerization is preferably carried out using Braid’s potassium permanganate method [103].

Diarylamines containing a tetrahydroquinoline, benzofuran, or benzozicin moiety have been used as antioxidants in a fully formulated Group II⁺ oil. The N-aryl-N-tetrahydroquinolinolamines gave the best performance in a bulk oil bench oxidation test [104]. Synergy was observed between one of these compounds and an alkylated diphenylamine [105].

A number of 4-nitro-4′-alkyldiphenylamines demonstrate significant antioxidant activity when used at 1.0–1.5 wt% in combination with 0.5 wt% alkylated diarylamines. The nitro compounds are inactive when used alone [106].
Aromatic diamines are a broad group of aminic antioxidants suitable for lubricants and fuels. N,N’-diphenyl-p-phenylenediamines where the phenyl groups may be substituted with methyl, ethyl, or methoxy groups have been claimed as effective antioxidants [107]. A broader range of substituted p-phenylenediamines have been claimed for crankcase lubricating oils for use in environments where iron-catalyzed oxidation reactions can take place [108]. Phenylenediamines have been claimed alone and in combination with other ashless antioxidants as a means of reducing soot-induced viscosity increase in diesel engines equipped with exhaust gas recycle (EGR) [109]. Substantial improvement in the pressurized differential scanning calorimetry (PDSC) oxidation induction time (OIT) was noted for gas-to-liquid (GTL) and PAO base oils stabilized with N,N’-bis(2,6-diisopropylphenyl)-p-phenylenediamine [110] and N,N’-bis(aryl)-ortho-phenylenediamines [111].

Michael reaction adducts of phenylenediamines [112] and tetraaryl hydrazines (Ar1Ar2N-N’Ar3Ar4) [113] gave good deposit control in fully formulated crankcase oils in the TEOST MHT test. Novel hydrazide antioxidants were prepared by treating phenylenediamine Michael adducts with hydrazine. Hydrazides were further maleated to prepare multifunctional dispersants [114].

Dispersants have been prepared incorporating aromatic amines, which might be expected to provide an antioxidant credit. Several patents report improvements in soot control and/or dispersancy, which may be due in part to better oxidation control [115–117]. However, a specific improvement in antioxidancy (PDSC OIT) is reported only in U.S. Patent 8,324,139, where the grafted amine is p-phenylenediamine [116].

Various 3,5-diethyltoluenediamines with the amino moieties being located on the 2,4- and 2,6-positions relative to the methyl group have been claimed to be effective in the prevention of oil viscosity increase and acid buildup [118]. The additives are relatively noncorrosive to copper and lead bearings and are compatible with seals at high temperatures and pressures. Tetraalkyl-naphthalene-1,8-diamines have been used in combination with alkylated diphenylamines or phenyl-naphthylamines as a lubricant antioxidant [119].

Some 2,3-dihydroperimidines can be prepared from the condensation of 1,8-diaminonaphthalenes with ketones or aldehydes and show good oxidation inhibition in the RVPOT (ASTM D2272). Synergistic behavior of the amines was also observed when an appropriate phenolic antioxidant is present [120]. Oils containing N,N’-disubstituted-2,4-diaminodiphenyl ethers and imines of the same ethers have shown low viscosity increase, low acid buildup, and reduced metal corrosion in bench tests [121,122].

Several antioxidant patents have been issued based on alkylated benzo triazole compounds. This class of antioxidant also has additional activity in the reduction of copper corrosion. Examples are N-t-alkylated benzo triazoles obtained by reacting a benzo triazole with an olefin such as diisobutylene [123] and the reaction products of a benzo triazole with an alkyl vinyl ether or a vinyl ester of a carboxylic acid such as vinyl acetate [124]. Antioxidant and antiwear properties were reported for benzotriazole adducts of an amine phosphate [125] or of organophosphorodithioate [126]. The former type also exhibited rust prevention characteristics in the ASTM D665 corrosion test. The reaction product of a hydrocarbyl succinic anhydride and 5-amino-triazole demonstrated antioxidant efficacy in a railway diesel oil composition [127].

1.6.2 Hindered Phenolic Compounds

Phenols, especially the sterically hindered phenols, are another class of antioxidants that are extensively used in industrial and automotive lubricating oils and greases. Based on chemical structure, phenols may be customarily categorized into simple phenols such as 2,6-di-tert-butyl-4-methylphenol (also known as BHT) and complex phenols that are typically in polymeric forms having molecular weights of 1000 or higher. The structures, important physical properties, and typical applications of some commonly used hindered phenols are given in Table 1.2.

Hindered phenols that incorporate sulfur atoms have been widely reported. The simplest are alkyl phenol sulfides. Alkyl phenols, such as mono- or dialkylated butyl-, pentyl-, or octyl-phenol, have been reacted with sulfur mono- or dichloride to form either mono- or disulfides [13,128–132]. The structure of a commercial sulfur-containing hindered phenol that has found use in various lubricant formulations is shown in Figure 1.4.

The reaction products of simple phenols, such as 2,6-di-tert-butylphenol, with selected thiokalenes have shown effectiveness in the prevention of acid buildup and oil viscosity increase, without causing lead corrosion [133]. Another patent describes a process for preparing alkylthio-substituted hindered phenols by reacting substituted phenols with hydrocarbyl disulfides using an aluminum phenoxide catalyst [134]. Using a 4,4’-methylene bis(2,6-di-tertiarybutylphenol) as reference, the (alkythio)phenols were found to be superior in a bulk oil oxidation tests and bench corrosion test on bearings. Reaction products prepared by sulfurizing mixtures of mono- and dialkylated sec- and tert-butyl phenols [135] and closely related high oligomeric phenolic antioxidants have been developed [136]. These compounds have lower volatility, better thermal stability, and improved seal compatibility and corrosion properties.

In general, sulfur-bridged hindered phenolics are more effective than the conventional phenolics under high-temperature oxidation conditions and are considered particularly suitable for the lubricants formulated with highly refined base oils [137]. Thioalkene-bridged hemi-hindered phenols prepared from the reaction of hindered phenols with thioalkenes have also been reported to be active in the stabilization of mineral oils and synthetic oils [133]. A number of antioxidants have been prepared, which combine a hindered phenol moiety with an ester that contains a sulfide linkage either β- to the phenolic ring or in the alkyl side chain [138,139].

Other hydroxybenzene compounds have been investigated recently. Hydroxychromans, including the general (Markush) structure illustrated in Figure 1.5, have been claimed as lubricant antioxidants [140].
### TABLE 1.2
Structure, Physical Properties, and Typical Applications of Commercial Hindered Phenols for Lubricants

<table>
<thead>
<tr>
<th>Phenols</th>
<th>Structure</th>
<th>Melting Point (°C)</th>
<th>Solubility (Minerals Oils)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,6-Di-tert-butyl-phenol</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>36–37</td>
<td>&gt;5</td>
<td>Industrial oils, power transmission fluids, greases, fuels</td>
</tr>
<tr>
<td>2,6-Di-tert-butyl-4-methylphenol (BHT)</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>69</td>
<td>&gt;5</td>
<td>Industrial oils, power transmission fluids, food-grade lubricants, greases</td>
</tr>
<tr>
<td>Tetrakis[methylene (3,5-di-tert-butyl-4-hydroxyphenyl) propionate] methane</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>110–125</td>
<td>0.1–0.5</td>
<td>Industrial oils, food-grade lubricants, greases</td>
</tr>
<tr>
<td>Octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>50–55</td>
<td>&gt;5</td>
<td>Industrial oils, eco-friendly oils</td>
</tr>
<tr>
<td>3,5-Di-tert-butyl-4-hydroxyhydrocinnamic acid, C₇–C₉ alkyl ester</td>
<td><img src="image5.png" alt="Structure" /></td>
<td>Liquid at 25°C</td>
<td>&gt;5</td>
<td>Industrial oils, power transmission fluids, greases, fuels</td>
</tr>
</tbody>
</table>

(Continued)
TABLE 1.2 (Continued)
Structure, Physical Properties, and Typical Applications of Commercial Hindered Phenols for Lubricants

<table>
<thead>
<tr>
<th>Phenols</th>
<th>Structure</th>
<th>Melting Point (°C)</th>
<th>Solubility (Minerals Oils)</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>3,5-Di-tert-butyl-4-hydroxyhydrocinnamic acid, C_{10–C_{16}} alkyl ester</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>Liquid at 25°C</td>
<td>&gt;5</td>
<td>Industrial oils, power transmission fluids, food-grade lubricants, greases</td>
</tr>
<tr>
<td>4,4′-Methylene bis(2,6-di-tert-butylphenol)</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>154</td>
<td>NA</td>
<td>Industrial oils, food-grade lubricants, greases</td>
</tr>
<tr>
<td>2,2′-Methylene bis(4-methyl-6-tert-butylphenol)</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>128</td>
<td>2–5</td>
<td>Industrial oils, eco-friendly oils</td>
</tr>
<tr>
<td>2-Propenoic acid, 3-[3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl]-1,6-hexanediyl ester</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>105</td>
<td>&lt;1</td>
<td>Industrial oils, greases, food-grade lubricants</td>
</tr>
</tbody>
</table>

FIGURE 1.4  A commercial sulfur-bridged phenolic antioxidant used in lubricants.

FIGURE 1.5  A generalized hydroxychroman antioxidant.
A group of C_{15}-substituted resorcinols derived from cashew nut shell liquid (CNSL) have been found to be effective antioxidants in crankcase formulations. The result is particularly intriguing, since the resorcinols are not hindered by substitution at the 2- and 6-positions [141]. A similar material, obtained by distillation of CNSL, followed by hydrogenation of the distillate, has been used as a stabilizer for trunk piston marine lubricants. When used in combination with overbased calcium salicylates, the composition also disperses asphaltene contaminants in the lubricant coming from the heavy fuel [142]. Note: CNSL has been reported in the literature as causing contact dermatitis [143].

1.6.3 MULTIFUNCTIONAL AMINE AND PHENOL DERIVATIVES

Given the effectiveness of both amine and phenol derivatives as lubricant antioxidants and the synergy between them (see Section 1.12), combining both functionalities in one molecule is a logical way to achieve synergistic performance. Ingold and Pratt have recently challenged the merits of this approach based on both net antioxidant costs and the likelihood that the relative stoichiometry of the two functionalities will be less than optimal [144].

The Mannich reaction was used to couple an ethoxylated alkyl phenol with an alkyl arylamine. The resulting products had markedly improved antioxidant activity relative to an equal weight loading of the amine alone and were noted as having improved solubility in oils [145]. Phenolic imidazolines have been prepared from polyaminophenols and carbonyl compounds [146]. In addition to providing antioxidant activity, the products also have corrosion inhibition and metal deactivation properties owing to the cyclic imidazoline moiety.

Multifunctional additives containing sulfur, nitrogen, and phenolic moieties in one molecule have been reported. In one instance, mercaptoenothiazoles or thiadiazoles are coupled by a Mannich reaction with hindered phenolic antioxidants to yield oil-soluble compounds with antioxidant and antiwear properties [147]. A more complex product having similar functionalities was obtained by reacting a sulfur-containing hindered phenolic ester with an alkylated diphenylamine [148]. Reaction products of polysobutenyl succinimide dispersants with hindered cinnamic acid esters have been claimed as dispersants with antioxidant functionality. The product reduced the formation of sludge and varnish deposits in the Sequence VG test (ASTM D6593) [149].

1.7 ORGANO COPPER ANTIOXIDANTS

The ability of copper compounds to function as oxidation inhibitors has been of interest to the lubricant industry for years. Copper is usually considered to be an oxidation promoter and its presence is of a concern in lubricants such as power transmission oils where fluid contact with copper-containing bearings, sintered bronze clutch plates, etc., takes place [150]. It has been suggested that copper corrosion products, originating from the surface attack of copper metal, are generally catalysts that accelerate the rate of oxidation [151], while oil-soluble copper salts are antioxidants [152]. To maximize the full antioxidant strength of a copper compound, the initial concentration needs to be maintained at an optimum range, normally from 100 to 200 ppm [150,152]. Below this range, the antioxidant effect of the copper compounds will not be fully realized, while above the range, interference with antiwear additives may occur, leading to pronounced increase in wear on high-stress contact points [153].

In early work, certain types of unsaturated hydrocarbons were sulfurized in the presence of copper. This produced a group of copper–sulfur complexes that are examples of oil-soluble copper antioxidants [154–156]. A more recent patent describes lubricant compositions that are stabilized with a zinc dihydrocarbyldithiophosphate (ZDDP) and 60–200 ppm of copper derived from oil-soluble copper compounds such as copper dihydrocarbyldithiophosphate or copper dithiocarbamates [153]. Oxidation data are given for fully formulated engine oils containing the ZDDP and a variety of supplemental antioxidants including amines, phenolics, a second ZDDP, and the copper salts. Only the blends with the copper salts passed the oxidation test. The viscosity increase was excessive with the other additives. Organocopper compounds including copper naphthenates, oleates, stearates, and polysobutylene succinimide hydrides have been reported to be synergistic with multi-ring aromatic compounds in controlling high-temperature deposit formation in synthetic base oils [152]. Oil-soluble copper compounds such as copper oleates, naphthenates, dithiocarbamates, or thiophosphates have also been reported to be synergistic with phenothiazines in controlling viscosity increase in lubricating oils [157].

More complex compounds obtained from further reactions of copper salts have also been reported to be effective antioxidants in a variety of lubrication applications. For example, copper carboxylate or copper thiocyanate was reacted with a mono-oxazoline, bis-oxazoline, or lactone oxazoline dispersant to form coordination complexes wherein the nitrogen contained in the oxazoline moiety is the ligand that complexes with copper. The resulting products exhibit improved varnish control and oxidation inhibition capabilities [158]. Reaction products of a copper salt (acetate, carbonate, or hydroxide) with a substituted succinic anhydride derivative containing at least one free carboxylic acid group are effective high-temperature antioxidants and friction modifiers. When incorporated in an engine oil formulation, the oil passed rust, oxidation, and bearing corrosion engine tests [159]. In another patent [160], a hindered phenolic carboxylic acid was used as the coupling reagent. The resulting copper compounds are reported to be effective in the control of high-temperature sludge formation and oil viscosity increase when used alone or in synergistic mixtures with a conventional amonic or phenolic antioxidant.

1.8 BORON ANTIOXIDANTS

The search for more eco-friendly additives to replace ZDDP has led to renewed interest in boron esters owing to their ability to improve antiwear, antifriction, and oxidative stability
properties of lubricants when used alone or in combination with other additives. A number of boron–oxygen-bearing compounds have been reported to be effective oxidation inhibitors in terms of the prevention of oil viscosity increase and acid formation at elevated temperature (163°C) [161–165]. Examples of these compounds include boron epoxides (especially 1,2-epoxyhexadecane) [161], borated single and mixed alkanediols [162], mixed hydroquinone-hydroxyster borates [159], phenol esters of hindered phenyl borates [164], and reaction products of boric acid with the condensates of phenols with aromatic or aliphatic aldehydes [165]. Appreciable oxidation inhibition effect has also been reported for borate esters of hydrocarbylene imidazolines [166], borates of mixed ethoxyamines and ethoxyamides [167], and borates of etherdiamines [168].

Borate esters with nitrogen (boron amides) are known for their improved antiwear properties, which are probably due to the formation of boron nitride films on the rubbing surfaces [169]. Borated adducts of alkyl diamines with long-chain hydrocarbylene alkoxides and low-molecular-weight carboxylic acids have been reported to have antifriction and antioxidant properties at elevated temperatures [170]. The treatment of inherently basic alkylamines with reactive boron compounds to form boron amides is known to improve the compatibility of the aminic compounds with engine seals [171,172].

Synergistic antioxidant effects of borate esters with alkylated diphenylamines or with zinc dithiophosphates have been established. When tested at 180°C in a PAO using a PDSC, strong synergistic antioxidant action was observed between borate esters and a dioctyldiphenylamine at a 1:1 (w/w) blending ratio [173]. A similar effect was observed for mixtures of borate esters and a ZDDP [174]. The synergy with ZDDP is of practical importance as it allows reduction in the phosphorus level in a finished lubricant without sacrifice of oxidative stability. The catalytic effect of boron in enhancing antioxidant performance has led to the development of phenolic-phosphorodithioate borates, obtained by borating a hindered phenol together with an alkyl phosphorodithioate-derived alcohol. The borates were found to possess exceptional antioxidant and antiwear activities. The synergy was proposed to arise from the formation of borate esters with both the hindered phenolic moiety and the phosphorodithioate alcohol within a single molecule [175].

Despite the many tribological and antioxidation benefits borate esters can offer, their use in lubricant applications has been limited. One serious drawback with most borate esters has been their high susceptibility to hydrolysis, a process that produces oil-insoluble and abrasive boracic acid. The following approaches have been taken to address the issue:

1. Incorporation of hindered phenolic moiety to sterically inhibit the boron–oxygen bonds from hydrolytic attack. Commonly used hindered phenolics are 2,6-diaryl phenols [176], 2,2’-thiobis(alkylphenols), and thiobis(alkynaphthols) [177].

2. Incorporation of amines that have nonbonding pairs of electrons. The amines coordinate with the electron-deficient boron atom, thus preventing hydrolysis. U.S. Patents 4,975,211 [178] and 5,061,390 [179] disclose the stabilization of borated alkyl catechol against hydrolysis by forming a complex with diethylamine. Significant improvement in hydrolytic stability was reported for borate esters, which incorporate an N,N’-dialkylamino-ethyl moiety [180]. It was hypothesized that the formation of a stable intramolecular five-member ring structure involving coordination of nitrogen with boron substantially inhibited hydrolytic attack by water.

3. Use of certain hydrocarbon diols or tertiary amine diols to react with boric acid to form stable five-member ring structures [181].

1.9 MISCELLANEOUS ORGANOMETALLIC COMPOUNDS

A number of oil-soluble titanium, zirconium, and manganese organometallic compounds have been claimed to be effective stabilizers for lubricants [182,183]. These materials include organic acid salts, amine salts, oxygenates, phenates, and sulfonates. Some of the compounds are essentially devoid of sulfur and phosphorus and therefore candidates for use in low-SAPS automotive engine oils. In one example [182], lubricating oils having 25 to ~100 ppm of titanium (derived from titanium (IV) isopropoxide) exhibited excellent oxidative stability in the high-temperature (280°C) Komatsu hot tube test and in the ASTM D6618 test that evaluates engine oils for ring sticking, ring and cylinder wear, and the accumulation of piston deposits in a four-stroke cycle diesel engine.

In another example [183], titanium (IV) isopropoxide was reacted with neodecanolic acid, glycerol mono-oleate, or polyisobutyl bis-succinimide to form the respective titanium compounds. These compounds, when used as a top treatment in a SAE 5W-30 engine oil so as to result in 50 to about 800 ppm of titanium, improved the deposit control capability of the oil as tested by the mid-high-temperature Thermo-Oxidation Engine Oil Simulation Test method (TEOST MHT, ASTM D7097). Similar antioxidant effects were observed for zirconium and manganese neodecanoates in the same oil. Synergistic antioxidant performance, as measured by an extended OIT, was observed in the PDCS test when titanium isopropoxide was used in combination with a hindered amine (bis(1,2,2,6,6-pentamethyl-1-piperidinyl)sebacate). The same patent also claims antioxidant formulations comprising similar hindered amines and molybdenum, tungsten, or boron compounds [184].

Amine tungstates and tungsten dithiocarbamates are soluble or dispersible in oil. They have been investigated as lubricant antioxidants and found to be synergistic with secondary diarylamines and/or alkylated phenothiazines. The mixtures are highly effective in controlling oil oxidation and deposit formation when they are added to an engine crankcase lubricant in an amount that results in ~20–1000 ppm of tungsten [185].

A formulation comprising an alkylated diphenylamine or an alkylated phenothiazine antioxidant and an ammonium
tungstate gave improved PDSC performance. The ammonium tungstate can be prepared from a polyisobutylene mono-
succinimide dispersant or dialkylamines [186]. This work has
been extended to include organomolybdenum compounds in
the formulation [187].

Sulfur-free molybdenum salts, such as molybdenum car-
boxylates, have been used as antioxidants and found to be
synergistic with alkylated diphenylamines in lubricating oils
[188]. The synergistic mixtures improved the oxidation stabil-
ity of crankcase lubricants while providing additional friction
modification characteristics. A sulfur- and phosphorus-free
fatty acid/molybdenum complex demonstrated antioxidant
synergy with di-tert-octyl diphenylamine in PAO, as mea-
sured by PDSC and Modified Penn State Micro-Oxidation
Test [189].

1.10 CONTROLLED RELEASE ANTIOXIDANTS

As new specifications continue to extend drain intervals for
lubricants, formulators want to guarantee that all additives are
present at sufficient levels throughout the service life. Once
the antioxidants in an oil have been exhausted, potentially
catastrophic viscosity increase will occur very quickly. A re-
cent approach to addressing this problem involves incorpo-
rating the additives into a controlled release carrier so that
fresh additive becomes available across the service life.

An additive gel containing dispersant/detergent and anti-
oxidant has been prepared. However, the additive gel must
still be introduced into the lubrication system separately from
the oil. This may be done through the use of a special gel-
charged oil filter or various types of metering addition devices
[190,191]. Another approach involves dispersing 0.01–50 μm
microcapsules containing a polar core and polar additive(s) in
an oil. The patent is prophetic for the use of antioxidants as
microencapsulated additives [192].

1.11 MECHANISMS OF HYDROCARBON
OXIDATION AND ANTIOXIDANT ACTION

Hydrocarbon-based lubricants undergo an oxidative process
called autoxidation, which leads to the formation of acids and
oil thickening. As the oil becomes increasingly degraded, oil-
insoluble sludge, deposits, and varnish may be formed, caus-
ing poor lubrication, reduced fuel economy, and increased
wear. Antioxidants are essential additives incorporated in
lubricant formulations to delay the formation of oxidation
products and keep the oil within specifications throughout
the service life. Mechanisms of lubricant degradation and the
stabilization of oils by antioxidants are discussed in the
following.

1.11.1 AUTOXIDATION OF LUBRICATING OIL

The well-documented autoxidation mechanism involves a
free-radical chain reaction [193–195]. It consists of four dis-
tinct reaction steps: chain initiation, propagation, branching,
and termination.

1.11.1.1 Initiation

\[ \text{RH} + \text{O}_2 \rightarrow \text{R}^* + \text{HOO}^- \]  \hspace{1cm} (1.1)
\[ \text{R}^- + \text{R}^* + \text{Energy} \rightarrow \text{R}^* + \text{R}^- \]  \hspace{1cm} (1.2)

The initiation step is characterized as the formation of free
alkyl radicals (R) from the breakdown of hydrocarbon bonds
by hydrogen abstraction and hemolytic cleavage of carbon–
carbon bonds. These reactions take place when hydrocarbons
are exposed to oxygen and/or energy in the form of heat, UV
light, or mechanical shear stress [196]. The ease of homolytic
cleavage of an R–H bond is determined by the C–H bond
strength and the stability of the resulting radical. Empirically,
the relative rates of hydrogen atom abstraction from carbon
have been found to be benzylic > allylic > tertiary > second-
ary > primary > phenyl [197,198]. Thus, hydrocarbons con-
taining tertiary hydrogen or hydrogen in an α-position to a
carbon–carbon double bond or aromatic ring are most sus-
ceptible to oxidation. The reaction rate of chain initiation is
generally slow under ambient conditions but can be greatly
accelerated with temperature and catalyzed by the presence of
transition metals (copper, iron, nickel, vanadium, manganese,
cobalt, etc.).

1.11.1.2 Chain Propagation

\[ \text{R}^- + \text{O}_2 \rightarrow \text{ROO}^- \]  \hspace{1cm} (1.3)
\[ \text{ROO}^- + \text{RH} \rightarrow \text{ROOH} + \text{R}^- \]  \hspace{1cm} (1.4)

The first propagation step involves an alkyl radical reacting
irreversibly with oxygen to form an alkyl peroxyl radical
(ROO•). This reaction is extremely fast and the specific rate
is dependent upon the radical’s substituents [193]. Once
formed, the peroxyl radical can readily abstract hydrogen
from another hydrocarbon molecule to form a hydroperoxide
(ROOH) and a new alkyl radical (R•). Therefore, each time a
free alkyl radical is formed, a large number of hydrocarbon
molecules may be oxidized to hydroperoxides.

1.11.1.3 Chain Branching

1.11.1.3.1 Radical Formation

\[ \text{ROOH} \rightarrow \text{RO}^- + \text{HO}^- \]  \hspace{1cm} (1.5)
\[ \text{RO}^- + \text{RH} \rightarrow \text{ROH} + \text{R}^- \]  \hspace{1cm} (1.6)
\[ \text{HO}^- + \text{RH} \rightarrow \text{H}_2\text{O} + \text{R}^- \]  \hspace{1cm} (1.7)

1.11.1.3.2 Aldehyde or Ketone Formation

\[ \text{RR}^*\text{HCO}^- \rightarrow \text{RCHO} + \text{R}^- \]  \hspace{1cm} (1.8)
\[ \text{RR}^*\text{CO}^- \rightarrow \text{RR}'\text{CO} + \text{R}^* \]  \hspace{1cm} (1.9)

The chain branching steps begin with the cleavage of a hydro-
peroxide into an alkoxy radical (RO•) and a hydroxy radic-
al (HO•). This reaction has a high activation energy and is
only significant at temperatures greater than 150°C. Catalytic
metal ions accelerate the process. The resulting radicals may
undergo a number of possible reactions: (1) the alkoxy radical abstracts a hydrogen from a hydrocarbon to form a molecule of alcohol and a new alkyl radical according to Reaction 1.6, (2) the hydroxy radical follows the pathway of Reaction 1.7 to abstract hydrogen from a hydrocarbon molecule to form water and a new alkyl radical, (3) a secondary alkoxy radical (RR′HCO•) may decompose via reaction pathway (1.8) to form an aldehyde, and (4) a tertiary alkoxy radical (RR′R′′CO•) may decompose to form a ketone (Reaction 1.9).

The chain branching reactions are very important to the subsequent condition of the oil. As a large number of alkyl radicals are formed, the oxidation process accelerates rapidly. The lower-molecular-weight alcohols, aldehydes, and ketones generated will immediately affect the physical properties of the lubricant by decreasing oil viscosity and increasing oil volatility and polarity. Under high-temperature oxidation conditions, the aldehydes and ketones can undergo further reactions to form acids and high molecular weight species that thicken the oil and contribute to the formation of sludge and varnish deposits.

1.11.1 Chain Termination

\[ \text{R}^\cdot + \text{R}^\cdot \rightarrow \text{R} - \text{R}^\cdot \quad (1.10) \]

\[ \text{R}^\cdot + \text{R}^\cdot \text{O}^\cdot \rightarrow \text{ROOR}^\cdot \quad (1.11) \]

As oxidation proceeds, oil viscosity will increase due to the formation of high-molecular-weight hydrocarbons. When the oil viscosity has reached a level where the diffusion of oxygen throughout the oil is significantly limited, chain termination reactions will dominate. As indicated by Reaction 1.10, two alkyl radicals can combine to form a hydrocarbon molecule. Alternatively, an alkyl radical can combine with an alkyl peroxyl radical to form a peroxide (Reaction 1.11). This peroxide, however, is not stable and can readily decompose to generate more alkyl peroxyl radicals. During the chain termination processes, formation of carbonyl compounds and alcohols may also take place via the peroxyl radicals that contain an abstractable α-hydrogen atom. This is illustrated in Figure 1.6 (Reaction 1.12).

1.11.2 Metal-Catalyzed Lubricant Degradation

Metal ions are able to catalyze the initiation step as well as the hydroperoxide decomposition in the chain branching step [199] via a redox mechanism illustrated in the following section. The required activation energy is lower for this mechanism, and thus the initiation and propagation steps can commence at much lower temperatures.

1.11.2.1 Metal Catalysis

1.11.2.1.1 Initiation Step

\[ \text{M}^{n+1}\text{R} \rightarrow \text{M}^n + \text{H}^+ + \text{R}^\cdot \quad (1.13) \]

\[ \text{M}^n + \text{O}_2 \rightarrow \text{M}^{(n+1)} + \text{O}_2^{−} \quad (1.14) \]

1.11.2.1.2 Propagation Step

\[ \text{M}^{(n+1)} + \text{ROOH} \rightarrow \text{M}^n + \text{H}^+ + \text{ROO}^− \quad (1.15) \]

\[ \text{M}^n + \text{ROOH} \rightarrow \text{M}^{(n+1)} + \text{HO}^− + \text{RO}^− \quad (1.16) \]

1.11.3 High-Temperature Lubricant Degradation

The preceding discussion describes the degradation of lubricants by autoxidation under both low- and high-temperature conditions. Low-temperature oxidation results in the formation of peroxides, alcohols, aldehydes, ketones, and water [200,201]. Under high-temperature oxidation conditions (>120°C), the decomposition of peroxides, including hydroperoxides, becomes predominant and the resulting carbonyl compounds (e.g., Reactions 1.8 and 1.9) will be oxidized to carboxylic acids. The carboxylic acids will start to consume the reserves of basic species provided by any overbased detergent/dispersant used in the formulation. As oxidation proceeds, acid- or base-catalyzed Aldol reactions take place [202]. Initially, α,β-unsaturated aldehydes or ketones are formed, and further condensation of these species leads to high-molecular-weight products. These products contribute to oil viscosity increase and eventually can combine with each other to form oil-insoluble polymeric products. These condensates can lead to sludge formation in a bulk oil oxidation environment or to varnish deposits on hot metal surface.

In a high-temperature study using the Penn State Micro-Oxidation test at 225°C, oxygenated polymeric species were observed to deposit on the test specimen in a single film. As soon as the film formed, it was observed to begin losing oxygen and hydrogen. Oxygenated deposits peaked early in the test, changing to black, largely carbon residue by the end [203]. Oil viscosity increase and deposit formation have been identified as being the principal oil-related causes of engine damage [204].

1.11.4 Effect of Base Oil Composition on Oxidative Stability

In the American Petroleum Institute (API) base oil classification system, mineral oils largely fall into the Groups I, II, III, and V categories, with some distinctions shown in Table 1.3 in terms of saturates, sulfur contents, and viscosity index. The market share

\[ \begin{align*}
\text{R}^\cdot + \text{R}^\cdot \text{O}^\cdot & \rightarrow \text{R}^\cdot + \text{R}^\cdot \text{O}^\cdot \\
\text{R}^\cdot + \text{O}_2 & \rightarrow \text{R}^\cdot + \text{O}_2^{−} \\
\text{R}^\cdot + \text{ROOH} & \rightarrow \text{R}^\cdot + \text{HO}^− + \text{RO}^− \\
\end{align*} \]

\[ \begin{align*}
\text{R}^\cdot + \text{R}^\cdot \text{O}^\cdot & \rightarrow \text{R}^\cdot + \text{R}^\cdot \text{O}^\cdot \\
\text{R}^\cdot + \text{O}_2 & \rightarrow \text{R}^\cdot + \text{O}_2^{−} \\
\text{R}^\cdot + \text{ROOH} & \rightarrow \text{R}^\cdot + \text{HO}^− + \text{RO}^− \\
\end{align*} \]

**FIGURE 1.6** Abstraction of α-hydrogen atoms to form ketones and alcohols.
of Group I base oils has dropped significantly over the last decade and now accounts for about 43% of global capacity. Meanwhile, the more highly refined Group II and Group III base oils have grown to 33% and 12% of global capacity, respectively [205].

It has been widely recognized that base oil composition, for example, linear and branched hydrocarbons, saturates, unsaturates, monoaromatics, polyaromatics, together with traces of nitrogen-, sulfur-, and oxygen-containing heterocycles, etc., plays an important role in the oxidative stability of the oil. There have been quite extensive research activities attempting to establish correlations between base oil composition and oxidative stability [206–210]. However, due to the large variations in the origin of the oil samples, the test methods, test conditions, and the performance criteria employed, the conclusions are not always consistent and in some cases are contradictory to each other. In general, it has been agreed that saturated hydrocarbons are more stable than the unsaturated toward oxidation. Of the different saturated hydrocarbons found in mineral oils, paraffins are more stable than cyclopentanes. Aromatic compounds, due to their complex and large variation in the chemical makeup, play a more profound role. Monocyclic aromatics are relatively stable and resistant to oxidation, while bi- and polycyclic aromatics are unstable and susceptible to oxidation [211]. Alkylated aromatics oxidize more readily due to the presence of highly reactive benzylic hydrogen atoms. Kramer et al. [208] demonstrated that the oxidation rate of a hydrocracked 500 N base oil doubled when the aromatic content increased from 1 to 8.5 wt%. Naturally occurring sulfur compounds are known antioxidants for the inhibition of the early stage of oil oxidation. Laboratory experiments have shown that mineral oils containing as little as 0.03% of sulfur had better resistance to oxidation at 165°C than sulfur-free white oils and PAOs [150]. In hydrocracked oils that are essentially low in aromatics, better oxidative stability was found with elevated sulfur concentration (above 80 ppm) versus a level at 20 ppm or lower [207]. It has been proposed that sulfur compounds act as antioxidants by generating strong acids that catalyze the decomposition of peroxides via a nonradical route or by promoting the acid-catalyzed rearrangement of arylalkyl hydroperoxides to form phenols that are antioxidants [150,193]. Contrary to sulfur, nitrogen-bearing compounds, especially the heterocyclic components (also called “basic nitrogen”), accelerate oil oxidation even at relatively low concentrations [212]. In highly refined Group II and III base oils that are essentially devoid of heteroatom-containing molecules, aromatic and sulfur contents are considered the main factors influencing the base oil oxidative stability [207,208]. It has been shown that the oxidative stability of a given base oil can be enhanced when the combinations and concentrations of base oil sulfur and aromatics have been optimized [209].

1.11.5 Oxidation Inhibition

There are two broad approaches to controlling lubricant oxidation: (1) the destruction of alkyl radicals, alkyl peroxy radicals, and hydroperoxides and (2) the trapping of catalytic metal impurities. These approaches can be implemented through the use of an appropriate antioxidant with radical scavenging or peroxide decomposing functionality and by using a metal deactivator, respectively.

The radical scavengers are known as primary antioxidants. They function by donating hydrogen atoms to terminate alkoxy and alkyl peroxy radicals, thus interrupting the radical chain mechanism of the autoxidation process. The key requirement for a compound to become a successful antioxidant is that peroxyl and alkoxy radicals abstract hydrogen from the compound much more readily than they do from hydrocarbons [213]. After hydrogen abstraction, the antioxidant becomes a stable radical and the alkyl radical becomes a hydrocarbon and the alkyl peroxy radical becomes an alkyl hydroperoxide. Hindered phenolics and aromatic amines are the two main classes of primary antioxidants for lubricants.

The peroxide decomposers are also called secondary antioxidants [194]. They function by reducing alkyl hydroperoxides in the radical chain to nonradical, less reactive alcohols. Organosulfur and organophosphorus compounds and those containing both zinc and phosphorus, such as zinc dialkylthiophosphates, are well-known secondary antioxidants.

Since transition metals are present in most lubrication systems, metal deactivators are usually added to lubricants to suppress the catalytic activities of the metals. Based on the mechanism of action, metal deactivators for petroleum products can be classified into two major types: chelators [194] and surface passivators [214]. The surface passivators act by attaching to a metal surface to form a protective layer, thereby preventing metal–hydrocarbon interaction. They can also minimize the corrosive attack of the metal surface by physically restricting access of the corrosive species to the metal surface. The chelators, on the other hand, function in the bulk of the lubricant by trapping metal ions to form an empirically inactive or much less active complex. With either mechanism, metal deactivators provide an antioxidant credit by effectively slowing the oxidation process catalyzed by the transition metals. Table 1.4 illustrates examples of metal deactivators that are commonly found in lubricant formulations.

1.11.6 Mechanisms of Primary Antioxidants

1.11.6.1 Hindered Phenolics

A representative example of a hindered phenolic antioxidant is 3,5-di-tert-butyl-4-hydroxytoluene (2,6-di-tert-butyl-4-methylphenol), also known as BHT. Figure 1.7 compares the reaction

---

<table>
<thead>
<tr>
<th>Table 1.3</th>
<th>API Base Oil Categories</th>
</tr>
</thead>
<tbody>
<tr>
<td>API Category</td>
<td>Percent Saturates</td>
</tr>
<tr>
<td>Group I</td>
<td>≤90</td>
</tr>
<tr>
<td>Group II</td>
<td>≥90</td>
</tr>
<tr>
<td>Group III</td>
<td>≥90</td>
</tr>
<tr>
<td>Group IV</td>
<td>PAOs</td>
</tr>
<tr>
<td>Group V</td>
<td>All other base oils not included in the first four groups (primarily napthenics and non-PAO synthetics).</td>
</tr>
</tbody>
</table>
rates of an alkyl radical with BHT and oxygen. The reaction rate constant \((k_2)\) of alkyl radical with oxygen to form alkyl peroxyl radicals is much greater than that \((k_1)\) of alkyl radical with BHT \([193,215,216]\). Hence with an ample supply of oxygen, the probability of BHT to react with alkyl radicals is low. As oxidation proceeds with more alkyl radicals being converted to alkyl peroxyl radicals, BHT starts to react by formally donating a hydrogen atom to the peroxyl radical as shown in Figure 1.8.

It has recently been proposed that this first step actually proceeds by a proton-coupled electron transfer (PCET) mechanism.

In this mechanism, a proton is transferred in a \(\sigma\)-bond fashion between heteroatoms (from one oxygen to another in this case), while an electron is simultaneously transferred from an orthogonal orbital on the phenol (generally perpendicular to the aromatic ring, allowing for \(2p-\pi\) overlap) to a singly occupied molecular orbital (SOMO) on the radical \([144]\). The steric hindrance provided by the two butyl moieties on the \textit{ortho}-positions effectively prevents the phenol radical from attacking other hydrocarbons \([215]\). The phenol radical can react with a second alkyl peroxyl radical to form a peroxyxyclohexadienone, which is stable at temperatures up to about 100°C–120°C \([216,217]\). Since each phenol molecule is capable of reacting with two radicals, the stoichiometric factor \(n = 2\) \([144,216]\).

Under higher-temperature oxidation conditions, the peroxyxyclohexadienone is no longer stable. As illustrated in Figure 1.9, it may decompose to form phenoxyl radical and an alkyl peroxyl radical, or alternatively to an alkyl radical, an alkoxy radical, and 2,6-di-\textit{t}-butyl-1,4-benzoquinone. As can be expected, the generation of new radicals will deteriorate the overall effectiveness of the BHT under high-temperature oxidation conditions.

### 1.11.6.2 Aromatic Amines

Alkylated aromatic amines have been of critical industrial importance as antioxidants for lubricants and rubber for over 60 years. While phenolic antioxidants sacrificially quench radicals in a stoichiometric manner, at temperatures above about 120°C, aromatic amines consume radicals and can then be regenerated as part of a catalytic cycle involving nitroxide radicals. Stoichiometric factors of \(n > 12\) have been reported \([201,218,219]\).

While many mechanisms have been proposed for the activity of amine antioxidants, until recently there have been very few studies that rise to the rigor of modern mechanistic organic chemistry. Jensen, Korcek, and coworkers published the landmark paper on the mechanism of aromatic amine antioxidants in 1995 \([219]\). In the last few years, there has been an outpouring of excellent calculational and experimental mechanistic work through collaborations of the Pratt and Valgimigli \([220,221]\) groups. Pratt et al. have proposed a novel refinement...
to the mechanism of amine antioxidants [218]. The very recent review by Ingold and Pratt discusses kinetics and mechanisms for aminic, phenolic, and other antioxidants [144].

The alkylated diphenylamines comprise a particularly effective class of aromatic amine primary antioxidants. The low-temperature (<100°C–120°C) reaction of the alkylated diphenylamine antioxidants begins with a formal hydrogen atom abstraction from the secondary amine by an alkyl peroxyl radical. The proposed overall mechanism for low-temperature reactions of aromatic amine antioxidants is illustrated in Figure 1.10. Transition state calculations have shown that as with phenols, the first step actually proceeds by a PCET mechanism. In the amine case, a proton is transferred from nitrogen to oxygen, while an electron is simultaneously transferred from a π orbital on the amine to a singly occupied π orbital on the radical [144,216,218,221]. The resulting aminyl radical can react with a second alkyl peroxyl radical, but decomposition of the peroxide intermediate results in the formation of a stable nitroxide and a highly reactive, chain-propagating alkoxy radical. However, the nitroxide is also an effective antioxidant.
It may react with an alkyl peroxy radical to sacrificially form an alcohol and a quinone nitroxy or potentially trap an alkyl radical. These termination steps combine to give a low-temperature stoichiometric factor \( n \) that is empirically about 2.

Reaction rates for N–H hydrogen atom abstraction by alkyl radicals have been determined at 100°C for DPA and several 4,4′-disubstituted alkylated diphenylamines [222]. N–H bond dissociation energies and relative reactivity toward alkyl, alkoxy, and peroxyl radicals (20°C–50°C) have been reported for DPA, alkylated diphenylamines, phenothiazines, and a few related structures. Trapping reactivity decreased \( \text{RO}^• > \text{ROO}^• > \text{R}^• \) [223].

At high temperatures (>120°C), the alkoxyamine becomes unstable, ultimately decomposing to form a ketone while regenerating the diphenylamine. The proposed catalytic mechanism for alkylated amines at high temperature is shown in Figure 1.11. Pratt and coworkers argue that the mechanism of alkoxyamine decomposition will vary depending upon whether the alkoxyamine R group is saturated (alkyl) or unsaturated (alkenyl). Alkyl radicals are proposed to decompose within a solvent cage by homolysis of the N–O bond, followed by disproportionation, while alkenyl radicals may undergo a novel retro-carbonyl-ene reaction [218]. Catalytic regeneration of the diphenylamine results in the high stoichiometric factors for ADPAs (\( n > 12 \)) relative to phenolics (\( n = 2 \)) cited previously. By-products such as the quinone nitroxy (Figure 1.10) remove ADPA from the cycle and prevent the cycle from continuing indefinitely [144].

1.11.7  *Mechanisms of Secondary Antioxidants*

1.11.7.1  **Organosulfur Compounds**

Organosulfur compounds function as hydroperoxide decomposers via the formation of oxidation and decomposition products. The reaction mechanisms have only been studied in detail for a rather limited number of the many organosulfur functionalities.

Phenothiazines, unsubstituted at nitrogen, were found to react with dioxetanes by single electron transfer, generating a phenothiazine radical cation and a dioxetane radical anion. The dioxetane radical anion may fragment or may abstract a hydrogen atom from the radical cation. Fragmentation is favored for the more stable radical cations (phenothiazine has low oxidation potential), while hydrogen atom abstraction is favored for less stable radical ions (phenothiazine has higher oxidation potential). Electron-donating groups lower the oxidation potential of the phenothiazine, hence reducing hydrogen atom transfer. N-alkyl phenothiazines were oxidized to sulfoxides [224].

Sulfoxides \( \text{RS(O)R} \) can decompose by a Cope elimination to form a sulfenic acid, \( \text{RSOH} \). Most sulfenic acids are too reactive to be isolated for direct use as an additive. The O–H bond of a sulfenic acid is very weak and readily donates H• to peroxyl radicals. The resulting \( \text{RSO}^• \) radical is stabilized by the sulfur atom [144].

At elevated temperatures, sulfenic acid (\( \text{RS(O)H} \)) may decompose to form sulfur dioxide (\( \text{SO}_2 \)), which is a particularly powerful Lewis acid for hydroperoxide decomposition through the formations of active sulfur trioxide and sulfuric acid. Previous work found that one equivalent of \( \text{SO}_3 \) was able to catalytically decompose up to 20,000 equivalents of cumene hydroperoxide [225].

1.11.7.2  **Organophosphorus Compounds**

Phosphites are important as ashless organophosphorus secondary antioxidants for lubricants. While phosphites can work synergistically with hindered phenolics, phosphites are less effective at chain termination. Phosphites can decompose hydroperoxides and peroxyl radicals following the reactions shown in the following. In these reactions, phosphite is oxidized to the corresponding phosphate, with the hydroperoxide and the peroxyl radical being reduced to alcohol and alkoxy...
Antioxidants

Mixtures of alkylated diphenylamines with phenothiazines hydroperoxides by reducing them to more stable alcohols. Enges radicals while the secondary antioxidant decomposes a secondary antioxidant. The primary antioxidant scavenes radicals while the secondary antioxidant decomposes a secondary antioxidant. The primary antioxidant scavenges radicals while the secondary antioxidant decomposes hydroperoxides by reducing them to more stable alcohols. Mixtures of alkylated diphenylamines with phenothiazines may function in a similar manner, with the phenothiazine functioning primarily as a peroxide decomposer via the reactive sulfur atom.

1.12 OXIDATION BENCH TESTS

Oxidative degradation of lubricants can be classified into two main reactions: bulk oil oxidation and thin-film oxidation. Bulk oil oxidation usually takes place at a slower rate in a larger oil body, such as a crankcase sump. The exposure to air (oxygen) is regulated by the surface contact kinetics and the gas diffusion is limited. Bulk oxidation leads to increases in oil acidity, oil thickening, and eventually the formation of oil-insoluble polymers. The polymers may combine with other impurities (metals, ash, water, partially burnt fuel, etc.), with the mixture dropping out of the oil collectively as sludge.

Thin-film oxidation describes a more rapid reaction in which a small amount of oil is exposed to severely elevated temperatures and air (oxygen). This may occur on the cylinder liner, for example. Under these conditions, hydrocarbons decompose much more quickly and the polar oil oxidation products formed at the oil–metal interface can rapidly build up on the metal surface, leading to the formation of varnish or deposits.

Fleet testing and fired engine tests are the best ways to evaluate lubricant performance. However, these tests are so expensive, labor intensive, and resource consuming that even the largest organizations use them selectively to validate leads drawn from bench tests.

Many oxidation bench tests have been developed over the years. These have proven to be valuable tools for lubricant formulators, particularly in the screening of new antioxidants and the development of new formulations. Most bench tests attempt to simulate the operating conditions of more expensive engine and field tests while taking into consideration either the bulk or thin-film oxidation conditions described previously. In addition, a third approach based on oxygen uptake in a closed system has been employed in some bench tests, such as the RPVOT (ASTM D2272) [229].

Due to the limitations of any laboratory setup, no single bench test can address all aspects of oxidation. The large variation in test conditions makes it rather difficult or even impossible to correlate one bench test with another. Furthermore, despite the best efforts of the test designers, the significance of proposed correlations between bench and engine tests is frequently the subject of spirited debate.

It is therefore common practice to run multiple tests at a time when characterizing a lubricant formulation and its additives. This section selectively reviews oxidation bench tests more closely related to the characterization of antioxidants. These tests have been standardized by some of the international standardization organizations such as ASTM International and the Co-ordinating European Council (CEC) and are widely used in the industry. It is important to note that there are a number of custom-tailored test methods designed for specific needs that have been proven to be advantageous in certain circumstances. The value of these tests should not be underestimated. A summary of the various tests is given in Table 1.5.

<table>
<thead>
<tr>
<th>Test</th>
<th>Test Designation</th>
<th>Oxidation Regime</th>
<th>Temperature (°C)</th>
<th>Gas</th>
<th>Gas Flow or Initial Pressure</th>
<th>Catalyst</th>
<th>Sample Size</th>
<th>End of Test</th>
<th>Parameter(s) Measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>PDSC</td>
<td>D6186</td>
<td>Thin film</td>
<td>130, 155, 180, 210</td>
<td>O₂</td>
<td>500 psi, 100 mL/m</td>
<td>None</td>
<td>3.0 mg</td>
<td>Occurrence of oxidation exotherm OIT</td>
<td></td>
</tr>
<tr>
<td>PDSC</td>
<td>CEC L-85</td>
<td>Thin film</td>
<td>210</td>
<td>Air</td>
<td>100 psi, no flow</td>
<td>None</td>
<td>3.0 mg</td>
<td>120 min max. OIT</td>
<td></td>
</tr>
<tr>
<td>TEOST</td>
<td>D6335</td>
<td>Bulk</td>
<td>100, 200–480</td>
<td>N₂O, moist air</td>
<td>3.6 mL/min</td>
<td>Fe naphthenate</td>
<td>116 mL</td>
<td>12 programmed cycles Deposits OIT</td>
<td></td>
</tr>
<tr>
<td>TEOST MHT</td>
<td>D7097</td>
<td>Thin film</td>
<td>285</td>
<td>Dry air</td>
<td>10 mL/m</td>
<td>Oil-soluble Fe, Pb, Sn</td>
<td>8.4 g</td>
<td>24 h</td>
<td></td>
</tr>
<tr>
<td>TFOUT</td>
<td>D4742</td>
<td>O₂ uptake, thin film</td>
<td>160</td>
<td>O₂</td>
<td>90 psig</td>
<td>Fuel, naphthenates of Fe, Pb, Cu, Mg, and Sn, H₂O</td>
<td>1.5 g</td>
<td>Deposits, volatile OIT</td>
<td></td>
</tr>
<tr>
<td>TOST</td>
<td>D943</td>
<td>Bulk</td>
<td>95</td>
<td>O₂</td>
<td>3.0 L/H</td>
<td>Fe, Cu, H₂O</td>
<td>300 mL</td>
<td>ΔTAN = 2.0 TAN, sludge, metal wt. loss</td>
<td></td>
</tr>
<tr>
<td>Dry TOST</td>
<td>D7873</td>
<td>Bulk</td>
<td>120</td>
<td>O₂</td>
<td>3.0 L/H</td>
<td>Fe, Cu</td>
<td>8 × 360 mL</td>
<td>D2272 residual, sludge, D2272 residual &lt;2.5%</td>
<td></td>
</tr>
<tr>
<td>IP 48</td>
<td>IP 48</td>
<td>Bulk</td>
<td>200</td>
<td>Air</td>
<td>15 L/H</td>
<td>None</td>
<td>40 mL</td>
<td>6 h × 2 Viscosity, carbon residue</td>
<td></td>
</tr>
<tr>
<td>IP 280/CIGRE</td>
<td>IP 280</td>
<td>Bulk</td>
<td>120</td>
<td>O₂</td>
<td>1 L/H</td>
<td>Cu, Fe naphthenates</td>
<td>25 g</td>
<td>164 h Volatile acids, oil acidity, sludge OIT</td>
<td></td>
</tr>
<tr>
<td>RPVOT</td>
<td>D2272</td>
<td>O₂ uptake</td>
<td>160</td>
<td>O₂</td>
<td>90 psig</td>
<td>Cu, H₂O</td>
<td>50 mL</td>
<td>ΔP = 25 psi</td>
<td></td>
</tr>
</tbody>
</table>
1.12.1 **Thin-Film Oxidation Tests**

1.12.1.1 **Pressurized Differential Scanning Calorimetry (PDSC)**

Differential scanning calorimetry, including PDSC, is a thermal technique for rapid and accurate determination of thermal-oxidative stability of base oils and performance of antioxidants. PDSC has been a more sought-after technique for two main reasons. First, high pressure elevates boiling points, thus effectively reducing experimental errors caused by volatilization losses of additives and the light fractions of base oil; second, it increases the saturation of the reacting gases in sample, allowing the use of lower test temperature or shorter test time at the same temperature [230].

PDSC experiments can be run in an isothermal mode to measure OIT corresponding to the onset of oil oxidation or in a programmed temperature mode to measure the onset temperature of oxidation. The temperature technique has been utilized to study the deposit-forming tendency of five engine oils, and the results obtained were consistent with their engine test ranking [231]. The OIT technique, however, is more commonly used for its simplicity and speed. Its early use can be traced back to the 1980s when Hsu et al. [232] tested a number of engine oils and found the induction periods of the samples to be indicative of the Sequence IIID viscosity break points. Soluble metals consisting of lead, iron, copper, manganese, and tin together with a synthetic oxidized fuel were included as catalysts to promote oil oxidation.

The CEC L-85 and the ASTM D6186 [233,234] are two standard methods that are based on OIT technique. Key test conditions of the methods are collected in Table 1.5. The CEC L-85 test method was originally developed for European ACEA (Association des Constructeurs Européens de l’Automobile) E5 specification for heavy duty diesel oils and has been incorporated in the current E7 and E9 specifications. The test is capable of differentiating between different quality base oils, additives, indicating antioxidant synergies and correlating with some bulk oil oxidation tests [235,236]. With appropriate modifications to the standard methods, PDSC has been successfully utilized in the characterization of a variety of lubricants in addition to automotive engine oils. These include, but are not limited to, base oils [237,238], greases [239], turbine oils [238], gear oils [240], synthetic ester lubricants [241], and biodegradable oils [242,243]. Using PDSC to study the kinetics of base oil oxidation [244] and antioxidant structure–performance relationship [245] has also been reported.

1.12.1.2 **Thermo-Oxidation Engine Oil Simulation Test (TEOST, ASTM D6335; D7097)**

The TEOST was originally developed to assess the high-temperature deposit forming characteristic of API SF quality engine oils under turbocharger operating conditions [246]. The original test conditions were specified as the 33C protocol and subsequently standardized in the ASTM D6335 method [247]. In this test, oil containing ferric naphthenate is in contact with nitrous oxide and moist air and is cyclically pumped to flow past a tared depositor rod. The rod is resistively heated through 12 temperature cycles, each going from 200°C to 480°C for 9.5 min. After the heating cycle is complete, the deposit formed on the depositor rod is determined by differential weighting. The 33C protocol was found capable of discriminating engine oils with known ability in resisting deposit formation in critical areas of engines [246].

The successful use of high-temperature deposition test to characterize engine oils has led to the development of a TEOST MHT protocol, a simplified procedure for the assessment of oil deposition tendency in the piston ring belt and under-crown areas of fired engines [248]. Thin-film oxidation condition was thought to be predominant in these areas, and accordingly, the depositor assembly was revised to allow the oil to flow down the rod in a slow and even manner to obtain a desired thin film. To better reflect the thermal-oxidative conditions of the engine zone of interest, a continuous depositor temperature of 285°C together with modified catalyst package and dry air are employed. The test runs for 24 h, and afterward, the amount of deposits formed on the tared depositor is gravimetrically determined [249]. Since introduction, the TEOST MHT has been incorporated in the ILSAC GF-3 through GF-6 engine oil specifications with an upper limit of 45 and 35 mg, respectively. Aside from being a thermo-oxidation test, TEOST can also be used to characterize neutral and overbased detergents of automotive engine oils [250].

1.12.1.3 **Thin-Film Oxygen Uptake Test (TFOUT, ASTM D4742)**

The TFOUT method was originally developed under the U.S. Congress mandate to monitor batch-to-batch variations in the oxidative stability of re-refined lubricating base oils [251]. The test heats a small amount of oil to 160°C in a high-pressure reactor pressurized with oxygen, along with a metal catalyst package, a fuel catalyst, and water to partially simulate the high-temperature oxidation conditions in automotive combustion engines [252]. Better oxidative stability of oil corresponds to a longer time taken to observe a sharp drop in oxygen pressure. TFOUT can be carried out in a RPVOT apparatus upon proper modification to the sampling accessories. Based on the results obtained from testing a limited number of reference engine oils, qualitative correlation between TFOUT and the Sequence IIID engine dynamometer test has been established [253]. Since being adopted as an ASTM standard method, there has been a wider utilization of the TFOUT to screen lubricants, base oils, and additive components prior to Sequence III engine testing [251].

1.12.2 **Bulk Oil Oxidation Tests**

1.12.2.1 **Turbine Oil Stability Test (TOST, ASTM D943, D4310, Dry TOST D7873)**

The turbine oil stability test (TOST) has been widely used in the industry to assess the oxidative stability of inhibited steam turbine oils under long-term service conditions. It can be used on other types of industrial lubricants such
as hydraulic fluids and circulating oils and in particular on those that are prone to water contamination in service. The test runs at relatively low temperature (95°C) to represent the thermal-oxidative conditions of real steam turbine applications. Two versions of the TOST, namely, ASTM D943 and D4310, have been developed [254,255]. Both methods share some common test conditions including test apparatus, catalysts, sample size, temperature profile, and gas, with minor differences in the test duration and target oxidation parameters to be monitored. The ASTM D943 measures oxidation lifetime, which is the number of hours required for the test oil to reach an acid number of 2.0 mg KOH/g or above. The ASTM D4310 determines the sludging and corrosion tendencies of the test oil by gravimetrically measuring oil-insoluble products after 1000 h of thermal and oxidative stress. The total amount of copper in the oil, water, and sludge phases is also determined.

A modified TOST method that operates at higher temperature (120°C) and in the absence of water was proposed [256] and recently became ASTM D7873 (Dry TOST method) [257]. The procedure requires RPVOT as a monitoring tool and is specifically suitable for the determination of sludging tendencies of long-life steam and gas turbine oils formulated with the more stable Group II and III base oils and high-performance aminic antioxidants. The Dry TOST method is a potential alternative to the original methods that have found to be less discriminatory on such high-performance turbine oils.

1.12.2.2 IP 48 Method

The Energy Institute IP 48 is a high-temperature bulk oil oxidation test that was originally designed for the characterization of base oils [258]. The test stresses a 40 mL sample of oil in a glass tube at 200°C, along with air bubbling at 15 L per h, for two 6 h periods with a 15–30 h standby period in between. Oil viscosity increase and the formation of carbon residue are determined after the oxidation. The test is considered unsuitable for additized oils (other than those containing ashless additives) or those that form solid products or evaporate more than 10% by volume during the test. However, successful assessment of engine oils using a modified IP 48 method with four 6 h cycles has been reported [258,259].

1.12.2.3 IP 280/CIGRE

The IP 280, also known as the CIGRE test, was designed to assess the oxidative stability of inhibited mineral turbine oils, targeting formations of volatile acid products (via water absorption), sludge, and increase of oil acidity [260]. The IP 280 and the TOST D943 are similar to each other in terms of the oxidation regime employed. However, the test conditions are different. Therefore, it is common practice to conduct both tests, since the limits for each test are stipulated in some turbine oil specifications. The IP 280 was found to be more suitable for discriminating performance of additive packages, while the D943 is more suitable for comparative evaluation of base oils derived from different crude source and processing techniques [261].

1.12.3 Oxygen Uptake Test

1.12.3.1 Rotating Pressure Vessel Oxidation Test (RPVOT, ASTM D2272)

The RPVOT, originally known as the Rotating Bomb Oxidation Test, was designed to monitor the oxidative stability of new and in-service turbine oils having the same composition. It can also be used to characterize other types of industrial lubricants, for example, hydraulic fluids and circulating oils. The test utilizes a steel pressure vessel where sample oil is initially pressurized to 90 psi with oxygen and thermally stressed to 150°C in the presence of water and copper coil catalyst until a pressure drop of 25 psi is observed [262]. The test temperature was chosen in order to promote measurable oil breakdown in a relatively short time. However, this temperature means that the test is not representative of most steam turbines that operate below 100°C or to the combustion turbines that operate at much higher temperatures [263]. Due to its sensitivity to specific additive chemistries, RPVOT finds limited use in comparing differently formulated oils. In addition, the test is more suitable for the determination of remaining useful life of in-service turbine oils rather than the qualification of new oils. Efforts to correlate RPVOT to the lengthy TOST D943 on steam turbine oils have been successful, suggesting that the results from RPVOT may be used to estimate the relative lifetime of turbine oils in the TOST D943 [264].

1.12.4 Experimental Observations

The following two experiments demonstrate (1) the comparative performance of an alkylated aminic antioxidant (ADPA) versus a hindered phenolic that is in agreement with the mechanisms discussed previously and (2) how proper selection and combinations of antioxidants can lead to synergy that further enhances performance.

In the first experiment, two turbine oils each formulated with a base oil selected from an API Group I or Group IV base oil, a standard additive package of metal deactivator and corrosion inhibitor, and 0.8 wt% of the antioxidants of interest were tested by using the TOST D943 lifetime method. The aminic antioxidant was an alkylated diphenylamine containing a mixture of butylated and octylated diphenylamines. The hindered phenolic was a C_{17}-C_{20} branched alkyl ester of 3,5-di-tert-butyl-4-hydroxyhydrocinnamic acid. As can be seen from the TOST results shown in Figure 1.13, in either oil the hindered phenolic significantly outperformed the alkylated diphenylamine by providing longer protection time against oxidation. Mixtures of the alkylated diphenylamine and the hindered phenolic at 0.4 wt% each in the oils provided even stronger protection, leading to an extended lifetime of about 5000 h for the Group I turbine oil and well over 8000 h for the Group IV turbine oil. Thus, under the low-temperature test conditions, the hindered phenolic was superior to the alkylated diphenylamine. Using the correct combination of the two additives produced synergy offering the maximum protection.
In the second experiment, a turbine oil formulated with an API Group I base oil, a metal deactivator, a corrosion inhibitor, and a 0.5 wt% of the same antioxidants as before was tested by using the RPVOT (ASTM D2272). The results are graphically presented in Figure 1.14. At the higher test temperature (150°C), the OIT of the blend containing alkylated diphenylamine was about 600 min, at which time the alkylated diphenylamine was depleted. The hindered phenolic protected the oil for about 300 min, indicating the hindered phenolic is only half as effective as the alkylated diphenylamine under the same test conditions. A mixture of alkylated diphenylamine and hindered phenolic with 0.25 wt% of each additive present provided a protection for over 700 min. Therefore, in contrast to the TOST results, under high-temperature conditions the alkylated diphenylamine was superior to the hindered phenolic. Similar to what was observed in the TOST, a synergistic mixture of the two additives provided the maximum protection.

The superiority of alkylated diphenylamine over hindered phenolic and the benefit of antioxidant synergy for maximum oxidation protection have been further demonstrated in a GF-4 prototype passenger car motor oil (PCMO). The oil contained an API Group II base oil, a low level (0.05 wt%) of phosphorus derived from ZDDP, and a number of other additives (detergents, dispersant, viscosity index improvers, pour point depressant, etc.) that are commonly found in engine oil formulations. The alkylated diphenylamine, hindered phenolic, and their mixture were tested at 1.0 wt% in the oil on a TEOST MHT apparatus using the ASTM D7097 standard procedure. The results are presented in Figure 1.15.
Lubricant Additives: Chemistry and Applications

The baseline blend, which contained all other additives except the antioxidant, produced a fairly high level (130 mg) of deposits. With the addition of the hindered phenolic, the deposit was substantially reduced to about 80 mg, and with the alkylated diphenylamine down to about 55 mg. By properly mixing the two antioxidants together while keeping the total level constantly at 1.0 wt%, the deposit was further reduced to about 40 mg. The TEOST results confirm the superior performance of alkylated diphenylamine and further demonstrate the benefit of antioxidant synergy for high-temperature oxidation conditions.

The antioxidant mechanisms discussed earlier well explain the experimental results and can serve as a foundation to guide lubricant formulators in the selection of correct antioxidant(s) for a particular end use. In order to obtain a successful formulation, other factors such as cost/performance, volatility, color, solubility, odor, physical form, toxicity, and compatibility with other additives need also be taken into consideration. From a performance standpoint, hindered phenolics are excellent primary antioxidants for their stoichiometric reactions with free radicals under lower-temperature conditions. In contrast, alkylated diphenylamines are excellent primary antioxidants for high-temperature conditions owing to their catalytic radical scavenging actions. As demonstrated, the synergy between the alkylated diphenylamine and the hindered phenolic is significant in the inhibition of oil oxidation. It is, however, important to note that the generation and the magnitude of an antioxidant synergy are dependent on the formulation, base oil, and test method used. The alkylated diphenylamine/hindered phenolic synergy is fairly robust as it was successfully reproduced in two oil formulations and found to be synergistic with alkylated diphenylamine in low-phosphorus engine oils [265]. Several instances of other types of synergy have been demonstrated and discussed in greater depth elsewhere. These include, but are not limited to, the synergy between sulfur-bearing hindered phenolic and alkylated diphenylamine antioxidants for hydrotreated base oils [137,266], between different aminic antioxidants [267], and between primary antioxidants and organophosphites [55].

1.13 ANTIOXIDANT PERFORMANCE WITH BASE OIL SELECTION

Driven by ever-increasing environmental and performance requirements, the lubricant industry is rapidly changing for the better with the advances of additive and base oil technologies. One notable change from a formulation point of view is that the conventional solvent-extracted base oils (Group I) are increasingly being replaced by higher-quality, higher-performance Group II and III base oils made from hydrotreated (hydrocracked), hydrotreating, and hydrocatalytic dewaxing and GTL processes. These processes provide oils with low sulfur, high degree of saturation, and viscosity index (Table 1.3). Lubricants formulated with these base oils generally have improved performance characteristics such as superior oxidative stability, lower volatility, improved low-temperature properties, longer drain intervals, and improved fuel economy. Because of these benefits, the API Group III base oils are becoming a serious challenge to synthetic PAOs for top-tier oil formulations.

Many efforts have been made to understand the relationship between the base oil composition and the response to added antioxidants. Such knowledge is extremely important for lubricant formulators when it comes to the selection of an appropriate antioxidant system for a given oil. Figure 1.16 shows the RPVOT results of four base oils with and without the presence of an antioxidant. Each oil represents...
Antioxidants

an API Group from I to IV. The hindered phenolic and the alkylated diphenylamine are the same as in Section 1.12. Clearly, without the protection of antioxidant, all oils performed equally poorly. A 0.5 wt% loading of the hindered phenolic antioxidant gave modest levels of protection that marginally increased from API Group I to API Group IV. When the base oils were treated with the same level of the alkylated diphenylamine, a dramatic performance boost is seen across the board. The improvement in performance of the highly refined Groups II, III, and IV to the added alkylated diphenylamine appears to be particularly strong. The superior antioxidant response of the Group II and III base oils over the conventional Group I base oils may be attributed to the removal of aromatic hydrocarbons and polar constituents and the large presence of saturated hydrocarbons in the oils [268,269].

ZDDP, another important class of antioxidant/antiwear agent, has been studied by others, and the results indicated that its antioxidant performance is dependent on the base oil aromatics, alkyl-substituted aromatics, average chain length of hydrocarbons, and the relative presence of normal paraffins and isoparaffins [211]. In Group I base oils, ZDDP gave good responses to highly saturated hydrocarbons characterized with normal paraffins having shorter chain length. Isoparaffins were found to decrease the antioxidant activity of ZDDP due to the steric hindrance of the side chains, which restricts the additive molecules from interacting with the hydrocarbons. In oils with higher monoaromatic hydrocarbons, ZDDP tends to perform better, which was believed to be related to improved solvency.

1.14 FUTURE REQUIREMENTS

The petroleum industry is currently working through the effects of nonconventional drilling and hydraulic fracturing, the disruptive new technologies commonly referred to as “fracking.” The rapid development of the shale-gas industry has made possible the ready availability of higher-quality base oils from GTL processes [270]. With crude oil prices depressed, there is presently less incentive for investment in biobased lubricant and energy sources.

However, despite the new sourcing options for petrochemicals, the need to meet environmental regulations remains unchanged. Lubricant formulators face continued pressure to reduce the already low levels of sulfur, phosphorus, zinc, and other metals present in their oils, in order to safeguard and improve the operation of emissions control systems.

Engine and vehicle OEMs continue to press for ever extending oil drain intervals, for customer convenience, oil conservation, and waste minimization [270]. The amount of ashless antioxidants used in engine oils may increase. However, there can be a limit to the amount of antioxidant (and other additives) that can be added to a formulation, and the higher-quality base oils likely to be used in these formulations tend to be less effective in dissolving additives and oxidation products than lower-grade oils. Therefore, there will be a continuing need for developing more effective antioxidants and/or antioxidant combinations.

The most pressing challenge facing the automotive industry today comes in the area of fuel economy, with mandated CAFE requirements of 54.5 mpg by 2025 [271]. Lubricants must contribute to this goal. Fuel economy is measured in the proposed GF-6 standard by the Sequence VI-D test (ASTM D7589) or its equivalent [272] (Sequence VI-E, in development).

Over the last 30 years or so, the primary approach to improving the lubricant contribution to fuel economy has been to reduce viscosity. Whereas SAE 10W-30 was the primary PCMO viscosity grade in 2000, 5W-30 and 5W-20 grades dominate today [273]. The viscosity reduction trend continues, with the recent introduction of specifications for SAE 0W-16, 0W-12, and 0W-8 grades [274,275]. With the reduction in oil film thickness that accompanies lowered viscosity, we expect that these very low viscosity oils will behave in an increasingly boundary lubrication mode. These oils will require excellent antioxidant protection for deposit control and further protection with friction modifiers.

**FIGURE 1.16** RPVOT results of hindered phe nolic and alky lated diphenylamine in API Group I to IV base oils.
### 1.15 SOME COMMERCIAL ANTIOXIDANTS

<table>
<thead>
<tr>
<th>Product</th>
<th>Company</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irganox® L 06</td>
<td>BASF</td>
<td>Octylated phenol-α-naphthylamine</td>
</tr>
<tr>
<td>Irganox® L 57</td>
<td>BASF</td>
<td>Butylated, octylated diphenylamine</td>
</tr>
<tr>
<td>Irganox® L 64</td>
<td>BASF</td>
<td>Mixture of amine and high-molecular-weight phenolic antioxidants</td>
</tr>
<tr>
<td>Irganox® L 67</td>
<td>BASF</td>
<td>Dinonyldiphenylamine</td>
</tr>
<tr>
<td>Irganox® L 101</td>
<td>BASF</td>
<td>Pentaeathyrotil tetrakis(3-(3,5-di tert-butyl-4-hydroxyphenyl) propionate)</td>
</tr>
<tr>
<td>Irganox® L 107</td>
<td>BASF</td>
<td>Octadecyl 3-(3,5-di tert-butyl-4-hydroxyphenyl)propionate</td>
</tr>
<tr>
<td>Irganox® L 109</td>
<td>BASF</td>
<td>Hindered bis-phenol: [2-Propenoic acid, 3-[3,5-bis(1,1-di methyl-ethyl)-4-hydroxyphenyl]-, 1,1'-(1,6-hexanediyl) ester]</td>
</tr>
<tr>
<td>Irganox® L 115</td>
<td>BASF</td>
<td>2,2'-Thiodiethylene bis-(3,5-di tert-butyl-4-hydroxyphenyl)propionate</td>
</tr>
<tr>
<td>Irganox® L 135</td>
<td>BASF</td>
<td>3,5-Di tert-butyl-4-hydroxy-hydrocinnamic acid, C₇–C₉ alkyl ester</td>
</tr>
<tr>
<td>Irgafos® 168</td>
<td>BASF</td>
<td>Tris(2,4-di tert-butyphenyl) phosphate</td>
</tr>
<tr>
<td>Naugalube® 438</td>
<td>Chemtura</td>
<td>Dioctyldiphenylamine</td>
</tr>
<tr>
<td>Naugalube® 438L</td>
<td>Chemtura</td>
<td>Dinonyldiphenylamine</td>
</tr>
<tr>
<td>Naugalube® 750</td>
<td>Chemtura</td>
<td>Butylated-, octylated-diphenylamine</td>
</tr>
<tr>
<td>Naugalube® AMS</td>
<td>Chemtura</td>
<td>Alpha-methylstrenated DPA</td>
</tr>
<tr>
<td>Naugalube® APAN</td>
<td>Chemtura</td>
<td>Alkylated PANA</td>
</tr>
<tr>
<td>Naugard® PANA</td>
<td>Chemtura</td>
<td>Phenyl-alpha-naphthylamine</td>
</tr>
<tr>
<td>Additin® RC 7001</td>
<td>Rhein Chemie</td>
<td>Polymeric trimethylol-di hydroquinoline</td>
</tr>
<tr>
<td>Additin® RC 7010</td>
<td>Rhein Chemie</td>
<td>Phenyl-alpha-naphthylamine</td>
</tr>
<tr>
<td>Additin® RC 7130</td>
<td>Rhein Chemie</td>
<td>Aminic antioxidant</td>
</tr>
<tr>
<td>Additin® RC 7132</td>
<td>Rhein Chemie</td>
<td>2,6-Di tert-butyl-p cresol</td>
</tr>
<tr>
<td>Additin® RC 7110</td>
<td>Rhein Chemie</td>
<td>Phenol derivative sterically hindered</td>
</tr>
<tr>
<td>Additin® RC 7115</td>
<td>Rhein Chemie</td>
<td>2,6-Di tert-butyl phenol</td>
</tr>
<tr>
<td>Additin® RC 7201</td>
<td>Rhein Chemie</td>
<td>Tetraakis[methylene(3,5-di tert-butyl-4-hydroxyphenyl) propionate] methane</td>
</tr>
<tr>
<td>Additin® RC 7207</td>
<td>Rhein Chemie</td>
<td>Octadeocyl-3-(3,5-di tert-butyl-4-hydroxyphenyl) propionate</td>
</tr>
<tr>
<td>Additin® RC 7209</td>
<td>Rhein Chemie</td>
<td>Hexamethylene bis[3-(3,5-di tert-butyl-4-hydroxyphenyl) propionate]</td>
</tr>
<tr>
<td>Additin® RC 7215</td>
<td>Rhein Chemie</td>
<td>Thiodiethylene bis[3-(3,5-di tert-butyl-4-hydroxyphenyl) propionate]</td>
</tr>
<tr>
<td>Additin® RC 7235</td>
<td>Rhein Chemie</td>
<td>Benzene propanoic acid, 3,5-bis-(1,1-di methyl-ethyl)-4-hydroxy-, C₇–C₉ branched alkyl esters</td>
</tr>
<tr>
<td>Ethanol® 4701</td>
<td>SIGroup</td>
<td>2,6-Di tert-butyl phenol</td>
</tr>
<tr>
<td>Ethanol® 4702</td>
<td>SIGroup</td>
<td>4,4’-Methylene bis-(2,6-di tert-butyl phenol)</td>
</tr>
<tr>
<td>Ethanol® 4716</td>
<td>SIGroup</td>
<td>3,5-Di tert-butyl-4-hydroxy-hydrocinnamic acid, C₇–C₉ alkyl ester</td>
</tr>
</tbody>
</table>

(Continued)

### 1.16 SOME COMMERCIAL METAL DEACTIVATORS

<table>
<thead>
<tr>
<th>Product</th>
<th>Company</th>
<th>Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Irgamer® 30</td>
<td>BASF</td>
<td>Triazole derivative</td>
</tr>
<tr>
<td>Irgamer® 39</td>
<td>BASF</td>
<td>Tolutariazole derivative</td>
</tr>
<tr>
<td>Irgamer® BTZ</td>
<td>BASF</td>
<td>Benzotriazole</td>
</tr>
<tr>
<td>Irgamer® TTZ</td>
<td>BASF</td>
<td>Tolutariazole</td>
</tr>
<tr>
<td>Cuvan® 303</td>
<td>RT Vanderbilt</td>
<td>N,N-bis(2-ethylhexyl)-ar-methyl-1H-benzotriazole-1-methanamine</td>
</tr>
<tr>
<td>Cuvan® 484</td>
<td>RT Vanderbilt</td>
<td>2,5-Dimeracapo-1,3,4-thiadiazole derivative</td>
</tr>
<tr>
<td>Cuvan® 826</td>
<td>RT Vanderbilt</td>
<td>2,5-Dimeracapo-1,3,4-thiadiazole derivative</td>
</tr>
<tr>
<td>Vanlube® 601</td>
<td>RT Vanderbilt</td>
<td>Heterocyclic sulfur-nitrogen compound</td>
</tr>
<tr>
<td>Vanlube® 601E</td>
<td>RT Vanderbilt</td>
<td>Heterocyclic sulfur-nitrogen compound</td>
</tr>
<tr>
<td>Vanlube® 704</td>
<td>RT Vanderbilt</td>
<td>Proprietary blend</td>
</tr>
</tbody>
</table>
REFERENCES


Antioxidants


Antioxidants


Yao, Y.B. The application of ashless thiocarbamate as lubricant antioxidation and extreme pressure additive. Lubricating Oil, 20(6), 41-44 (2005).


Zinc Dithiophosphates

Freuler, H.C. Modified lubricating oil. U.S. Patent 2,364,284 (December 5, 1944), Union Oil Co. of California.
Buckley, T.F. Methods for preventing the precipitation of mixed zinc dialkylidithiophosphates which contain high percentages of a lower alkyl group. U.S. Patent 4,577,037 (March 18, 1986), Chevron Research Co.

Dispersants

Komberekke, R.E. et al. Understanding soot-mediated oil thickening Part 6: Base oil effects. SAE Technical Paper 982, 665. Society of Automotive Engineers, October 1, 1998. Also see parts 1Bb by E. Bardasz et al., SAE Papers 952, 527 (October 1995), 961, 915 (October 1, 1996), 971, 692 (May 1, 1997), 976, 193 (May 1, 1997), and 972, 952 (October 1, 1997), Society of Automotive Engineers, Warrendale, PA.


Organic Friction Modifiers


Houben, M. Friction analysis of modern gasoline engines and new test methods to determine lubricant effects. 10th International Colloquium, Esslingen, Germany, 1996.


Battersby, J. , J.E. Hillier . The prediction of lubricant-related fuel economy characteristics of gasoline engines by laboratory bench tests. Proceedings of International Colloquium, Technische Akademie Esslingen, Ostfildern, Germany, 1996.


Selection and Application of Solid Lubricants as Friction Modifiers


Ashless Antiwear and Antiscuffing (Extreme Pressure) Additives


Macpherson, I. et al., NLGI Spokesman 60(1), 1996.


Lacey, I.N. et al., NLGI Spokesman 60(1), 1996.


Michaelis, K.P., and Wirth, H.O., Di- or triphosphonic acid diesters, U.S. Patent 4,244,827, 1981.


Selby, T.W., Development and significance of the phosphorus emission index of engine oils, Thirteenth International Colloquium on Tribology, Lubricants, Materials and Lubrication, Technische Akademie Esslingen, Ostfildern, Germany, January 15-17, 2002.

Selby, T.W., Fee, D.C., and Bosch, R.J., Analysis of the volatiles generated during the Selby-Noack test by 31P NMR spectroscopy, Elemental Analysis Symposium, ASTM D02 Meeting, Tampa, FL, December 2004.

Selby, T.W., Fee, D.C., and Bosch, R.J., Phosphorus additive chemistry and its effects on the phosphorus volatility of engine oils, Elemental Analysis Symposium, ASTM D02 Meeting, Tampa, FL, December 2004.


Ashless Phosphorus-Containing Lubricating Oil Additives

Williamson, S. Ann 92: 316, 1854.

Vogeli, F. Ann 69: 190, 1849.


Boerlage, G.D., H. Blok. Four-ball top for testing the boundary lubricating properties of oils under high mean pressures. Engineering 144 (July): 1, 1937.


Greenshields, R.J. Oil industry finds fuel additives can help in controlling pre-ignition. Oil Gas J 52(8): 71-72, 1953.


French Patent 681,1770, ICI, 1929.


U.S. Patent 5,584,201, Cleveland State University, 1986.


Metal Passivators, Newsletter No. 10, ADD APT AG, June 2000.


British Standard 3150, Corrosion-inhibited antifreeze for water-cooled engines, Type A. British Standard Institution, 1959.


Barber, R.I. The preparation of some phosphorus compounds and their comparison as load-carrying additives by the four-ball machine. ASLE Preprint 75-LC-2D-1, 1975.

Sulfur Carriers


G.W. Pressel, Base for metal-cutting methods and process of preparing the same, U.S. Patent 1,367,428, German Patent 129132, 1921.


M.G. van Voorhis, 200 lubricant additive patents issued in 1938 and 1939, National Petroleum News, 32, R-66, 1940.


L.R. Churchill, Lubricating Compound and process of making the same, U.S. Patent 1,974,299, 1939.


J.N. Borgen, Method of sulfurizing terpenes, abietyl compounds, etc., U.S. Patent 2,111,882, 1934.


J.B. Werder et al., Lubricating oil, U.S. Patent 1,971,243, 1932.


H.C. Mougay, G.O. Almen, Extreme pressure lubricants, ibid., 12, 76, 1931.


Schallbock et al., Vortrage der Hauptversammlung der deutschen Gesellschaft fűrMetallkunde, VDI Verlag, pp. 348B, 1938.


E.S. Forbes, Load carrying capacity of organo-Sulfur compounds review, Wear, Lausanne, 15, 341, 1970.


Typical Composition of Natural Oils and Fats, Flyer of the company Jacob Stern & Sons, Inc., Division Acme-Hardesty Co., Blue Bell, PA, 2016.
Chlorinated Paraffins

Comments from Chlorinated Paraffins Industry Association to EPA, Federal Register, March 2016.
G. Barrow , Wear of Cutting Tools, Tribology, 1972, 5, 228D.
V. A. Tipnis and J. D. Christopher , Machinability Testing and the Utilization of Machining Data, ASM, Metals Park, OH, 1979, pp. 3E6.

Olefin Copolymer Viscosity Modifiers

Carmen, C.J., R.A. Harrington, and C.E. Wilkes, Monomer sequence distribution in ethylene-propylene rubber measured by 13C NMR.
Hall, J.R., Ethylene, C3-16 monoolefin polymer containing 0.02%-0.6% by weight vinyl norbornene bound in the polymer having improved cold flow, US Patent 4156767 (1979).
Rotman, D., DuPont Dow debuts metallocone EPDM, Synthetic rubber, Chemical Week, p. 15, (May 14, 1997).
Kapuscinski, M.M. and L.D. Grina, Hydrocarbon compositions containing polyolefin graft polymers, European Patent 199453 (1986);
Chapelet, G., H. Knoch, and G. Marie, Novel lubricating compositions containing nitrogen containing hydrocarbon backbone polymeric additives, US Patent 5402255 (1997);
Engel, L.J. and J.B. Gardiner, Polymeric additives for fuels and lubricants, US Patent 4089794 (1978);
Waldbigill, J.O. and I.D. Rubin, Fatty alkyl succinateester and succinimide modified copolymers of ethylene and an alpha olefin, US Patent 4171273 (1979);
Hayashi, K., Multi-purpose additive compositions and concentrates containing same, US Patent 4320019 (1982);
Hayashi, K., Carboxylic acylating agents substituted with olefin polymers of high/low molecular weight mono-olefins, derivatives thereof, and fuels and lubricants containing same, US Patent 4489194 (1985);
Gutierrez, A. and D.Y. Chung, Multifunctional viscosity index improver derived from polyamine containing one primary amino group and at least one secondary amino group exhibiting improved low temperature viscometric properties, US Patent 5210146 (1992);
Chung, D.Y., A. Gutierrez, J.E. Johnston, M.J. Struglinski, and R.D. Lundberg, Multifunctional viscosity index improver derived from amido-amino copolymer, exhibiting improved low temperature viscometric properties, US Patent 5252238 (1993);
Chung, D.Y., A. Gutierrez, and M.J. Struglinski, Multifunctional viscosity index improver derived from amido-amine and degraded ethylene copolymer, exhibiting improved low temperature viscometric properties, US Patent 5290461 (1994);
Kievsky, T.E., EPR dispersant VI improver, US Patent 4189063 (1979);
Bloch, R., T.J. McCrary, Jr., and D.W. Brownwell, Ethylene copolymer viscosity index improver-dispersant additive useful in oil compositions, US Patent 4517104 (1985);
Gutierrez, A., D.W. Brownwell, R. Bloch, and J.E. Johnston, Ethylene copolymer viscosity index improver-dispersant additive useful in oil compositions, US Patent 4632769 (1986);
Lange, R.M., Dispersant-viscosity improvers for lubricating oil compositions, US Patent 5540851 (1998);
Nalesnik, T.E., Viscosity index improver, dispersant and anti-oxidant additive and lubricating oil composition containing same, European Patent 338672 (1989);
Nalesnik, T.E., Oil dispersant and antioxidant additive, European Patent 470698 (1992);
Kapuscinski, M.M. and T.E. Nalesnik, Dispersant, antioxidant and VI improver and lubricating oil composition containing same, European Patent 461774 (1991);
EPME/EPDM, Gosei Gomu, 95, 1B (1980).
Cozewith, C., S. Ju, and G.W. VerStrate, Copolymer compositions containing a narrow MWD component and process of making same, US Patent 4874820 (1989);
Polymethacrylate Viscosity Modifiers and Pour Point Depressants


Hydrogenated Styrene-Diene Copolymer Viscosity Modifiers

Zelluski R.P., Preparation of block copolymers in the presence of an organo-lithium catalyst and a solvent mixture comprising a hydrocarbon and an ether, thioether or amine, US 2975160, March 14, 1961.
Cui J., Oberoi S., Goldmints I., Briggs S., Field and bench study of shear stability of heavy duty diesel lubricants, SAE International.


Pour Point Depressants


Weiss, J., Biolubes: Cradle to Grave. ILMA Annual Meeting October 2011.
Evaluating Tackiness of Polymer-Containing Lubricants by Open-Siphon Method

V.G. Levich, Physico-Chemical Hydrodynamics (Russian), Fizmatgiz, Moscow, Russia (1959).

Seal Swell Additives

MIL-O-5606, Oil; hydraulic, aircraft, petroleum base, January 31, 1950.
MIL-H-5606G, Hydraulic fluid, petroleum base; aircraft; Missile and ordnance Notice 1, March 29, 1996.
MIL-PRF-50606H, Hydraulic fluid, petroleum base; Aircraft missile, and ordnance, June 7, 2002.
MIL-P-25732C Packing, preformed, petroleum hydraulic fluid resistant, limited service at 275°F (135°C), February 25, 1980.
MIL-P-25732C Packing, preformed, petroleum hydraulic fluid resistant, limited service at 275°F (135°C) Notice 1, November 15, 1989.
MIL-P-83461B, Packing, preformed, petroleum hydraulic fluid resistant, improved performance at 275°F (135°C), February 25, 1980.
MIL-R-83485, (USA), Rubber, fluorocarbon elastomer, improved performance at low temperatures, September 8, 1976.
MIL-H-87257, Hydraulic fluid, fire resistant; Low temperature, synthetic hydrocarbon base, aircraft and missile, March 2, 1992.
MIL-PRF-87257B, Hydraulic fluid, fire resistant; Low temperature, synthetic hydrocarbon base, aircraft and missile, April 22, 2004.

Antimicrobial Additives for Metalworking Lubricants

V.G. Levich, Physico-Chemical Hydrodynamics (Russian), Fizmatgiz, Moscow, Russia (1959).

Foaming Chemistry and Physics
Antifoams for Nonaqueous Lubricants


Corrosion Inhibitors and Burst Preventatives


Cohen, M., Inhibition of steel corrosion by sodium nitrate in water, J. Electrochem. Soc., 93(1); 26; 1948.
Hoar, T.P., Nitrite inhibition of corrosion: Some practical cases, Corrosion, 1, 103; 1954.
Bennett, E.O., D.L. Bennett, Metalworking fluids and nitrosamines, Tribol. Int., 17(6); 341; 1984.
Vukosavic, M.S., Rust protection of synthetic metalworking fluids with nitrite additives, Lubr. Eng., 40(9); 456; 1984.
Pante, C.J., Sodium replacementThe state of the art, Lubr. Eng., 35(11); 625; 1979.
Siddagangappa, S., S.M. Mayanna, F. Pushpanadan, 2,4-Dinitrophenylhydrazine as corrosion inhibitor for copper in sulphuric acid, Anti-Corros. Method. Mater., 23(8); 118; 1976.
Banweg, A., Organic treatment chemicals in steam generating systemsUsing the right tool in the right application, PowerPlant Chem., 8(3); 137; 2006.
Baker, R.F., F.F. Vaast, Sulfonates as corrosion inhibitors in greases, NLGI Spokesman, 57(11); 463; 1994.
Han, N., L. Shui, W. Lui, Q. Xue, Y. Sun, Study of the lubrication mechanism of overbased Ca sulfonates on additives containing S or P, Tribol. Lett., 14(4); 269; 2003.
Larson, R.G., G.L. Perry, Investigation of friction and wear under quasi-hydrodynamic conditions, Trans. ASME, 65(1); 456; 1945.
Desai, M.A., Corrosion inhibitors for aluminum alloys, Wessofte Korrrosion, 23(6); 475; 1972.
Alkylated Naphthalenes


# Additives for Bioderived and Biodegradable Lubricants


Terresolve Technologies In-house Knowledge Base.


Bergstra, R., Emerging opportunities for natural oil based chemicals, Plant Bio-Industrial Workshop, Saskatoon, Saskatchewan, Canada, February 27, 2007, MTN Consulting Associates, Edmonton, Alberta, Canada.

In-house Terresolve Technologies Proprietary Development Research, October 11, 2005 to January 8, 2007.


Erhan, S. Z., Oxidative stability of mid-oleic soybean oil: Synergistic effect of antioxidant and antiwear additives, National Center for Agricultural Utilization Research, USDA/ARS, Peoria, IL, 2006.429

# Additives for Grease Applications


Additives for Crankcase Lubricant Applications


Gergel, W. C., Detergents: What are they?, Presented at the JSLE/ASLE Meeting, Tokyo, Japan, June 10, 1975 (and references therein).

Kreuz, K. L., Gasoline engine chemistry as applied to lubricant problems, Lubrication, 55, 536, 1969.


Ingold, K. U., Inhibition of oil oxidation by 2,6-di-t-butyl-4-substituted phenols. Journal of Physical Chemistry, 64, 1636, 1960.


Johnson, M. D. , Korcek, S. , and Zimbo, M. , Inhibition of oxidation by ZDTP and ashless antioxidants in the presence of hydroperoxides at 160°C, SAE SP-558, pp. 31O381, 1983.


Lubricants and Fluids for the Food Industry


A. Breitner, 2015 nonfood compounds registration & ISO 21469 certification program update, NSF Steering Committee Meeting, Ann Arbor, MI, 2015.


P. Young, Food master food engineering section, A BNP media publication, Deerfield, IL, 2015.


Private communication from CPI Fluid Engineering Services, Midland, MI, 2016.

S. Lawate, Products for incidental food contact lubricants, Lubrizen 4300FG, Presented at the commercial forum, Society of Tribology and Lubrication Engineers (STLE) Annual Meeting, Philadelphia, PA, May 2017.


Private communication with Ryan Ritz of the Paratherm Heat Transfer Fluids, a Division of the Lubrizol Corporation, a Berkshire Hathaway company.


J. Spinnier, Low charge ammonia systems to hit US market, Food Production Daily, May 1, 2014.


ANSI/IIAR Standard, Published, September 2015.

A. Shiflet, Ammonia lubricants: Ensuring the proper usage of ammonia rated products in your everyday maintenance, RETA Conference, Milwaukee, WI, September 2015.

Lubricants for the Disk Drive Industry


D. Sianesi, V. Zamboni, R. Fontanelli, and M. Binagli, Perfluoropolyethers: Their physical properties and behavior at high and low temperatures, Wear, 18(2), 85-100 (1971).


Long-Term Trends in Industrial Lubricant Additives


**Eco Requirements for Lubricant Additives and Base Stocks**

United States Environmental Protection Agency, Environmental Acceptable Lubricants; EPA 800-R-11-002; Office of Wastewater Management; Washington, DC, November 2011.
Umweltbundesamt, LTWS-Schriftenreihe Nr. 12, Katalog wassergefährdender Stoffe, Umweltbundesamt, Berlin, Germany, 1996.
Bundesministerium für Verbraucherschutz, Ernährung und Landwirtschaft (Hrsg.), Bericht über schnell abbaubare Schmierstoffe und Hydraulikflüssigkeiten, June 2002.
RAL German Institute for Quality Assurance and Certification, Basic criteria for award of the environmental label: Readily biodegradable chain lubricants for power saw, RAL-UZ 48, edn., April 2007.
RAL German Institute for Quality Assurance and Certification, Basic criteria for award of the environmental label: Readily biodegradable lubricants and forming oils, RAL-UZ 64, edn., April 2007.
T. Röhe, Taylor-made lubricants by choosing the right base stocks AND the right additive: The component toolbox for lubricant formulations. Presentation given at the 19th International Colloquium Tribology, Technische Akademie Esslingen, Ostfildern, Germany, January 21□□□23, 2014.